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The Crystal Structure of Tetraethylammonium Trichlorooxo(1,1,1-trifluoro-4-thenoyl-2,4-butanedionato)niobate(V)

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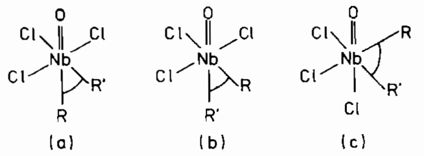
The structure of tetraethylammonium trichlorooxo(1,1,1-trifluoro-4-thenoyl-2,4-butanedionato)niobate(V) has been determined by single crystal X-ray analysis. Crystals are monoclinic: a = *12.495(2)* Å; b = *11.392(2)* Å; c = *16.940(3)* Å; β = *101.0(1)°; V = 2334* Å^3*; space group* $P2_1/c$*, Z = 4. The structure was solved from Patterson and electron density maps and refined by least-square methods to a conventional R value of 0.04 for 2409 independent non zero reflexions. The structure determination shows that the thenoyl group is* 'trans' *with respect to the Nb=O bond.*

Introduction

The trichlorooxo(trifluorothenoylbutanedionato)-niobate(V) as some other chelated hexacoordinated species of transition metals, exhibits the exchange phenomenon [1]. Fluorine n.m.r. spectra show two large CF_3 peaks consistent with the existence of two isomers at least in solution. This compound has been isolated as well characterized crystalline solid, and the crystal structure has been determined to point out what will be, of the three possible isomers a, b or c, the one occurring in the solid-state.



R = SC_5H_4; R' = CF_3

Experimental

X-ray Data Collection

Single crystals of parallelepiped habit were mounted in glove box under dry argon in lindeman glass capillary tubes. The crystal system and cell dimensions were determined from Weissenberg and precession (MoKα, λ = 0.71069) photographs and from single crystal diffractometry. Systematic extinctions h0l; l = 2n + 1 and 0k0; k = 2n + 1, indicated space group $P2_1/c$: a = 12.495(2) Å; b = 11.392(2) Å; c = 16.940(3) Å; β = 101.0(1)°; V = 2334 Å^3; Z = 4; D_m = 1.59 g cm^{-3}; D_c = 1.61 g cm^{-3}. Experimental density, D_m, was measured using floating technique with a tribromoethane–cyclohexane mixture.

A crystal of dimensions approximately 0.8 × 0.3 × 0.1 mm was selected for intensity measurements and was set up about |0 0 1| on a STOE 300 mm diameter eulerian craddle. MoKα radiation and a take-off angle of 3° were used with a graphite monochromator set in front of the counter. Power was supplied by a stabilized CGR Theta 60 generator. The scintillation counter was fitted with a pulse-height analyser adjusted to MoKα radiation in such a way that 90% of the diffracted intensity was counted.

The intensities of every independent reflexion with $\sin\theta/\lambda < 0.527$ were manually measured with an $\omega/2\theta$ scan. Scan range of 0.55° + 0.345tgθ was used with a scan speed of 0.7 deg min^{-1}. Background was measured for 15 seconds at both ends of scan in fixed position. Reflexions with counting rates greater than 10,000 c sec^{-1} were corrected for counting loss. The intensities of three standard reflexions 2 0 0, 0 1 4 and 0 0 10 were monitored at regular intervals (twice a day); no significant fluctuations were observed. Lorentz and polarization corrections were applied together with an absorption correction [2]. The absorption coefficient μ was determined to be 10 cm^{-1}; transmission factors ranged from 0.81 to 0.90. Each structure factor was assigned a standard deviation $\sigma = (F \times \Delta I)/I$ where I was the integrated intensity and ΔI the error on it. Of the 2623 independent reflexions 189 with structure factor F less than σ were not included in subsequent calculations.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) with Standard Deviations in Parentheses. The anisotropic temperature factor $T = \exp|-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)|$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	2149.7(3)	2596.4(4)	−431.1(2)	46.0(2)	41.6(3)	28.2(3)	−2.0(2)	8.2(1)	0.4(2)
Cl(1)	892(1)	4164(1)	−695.3(9)	63.2(8)	63.6(8)	77.6(9)	19.7(6)	0.3(7)	17.0(6)
Cl(2)	3262(1)	3702(1)	591.6(6)	64.2(7)	47.7(6)	37.8(6)	−3.0(5)	−0.0(6)	−7.7(5)
Cl(3)	3651(1)	1249(1)	−422.8(7)	64.1(8)	55.6(7)	69.9(8)	12.7(6)	23.3(6)	−10.8(6)
O	1471(3)	1752(3)	143(2)	64(2)	56(2)	53(2)	−3(2)	17(1)	6(1)
O(1)	3004(3)	3565(3)	−1317(2)	73(2)	64(2)	31(2)	−24(2)	16(1)	−6(1)
C(1)	3008(4)	3410(4)	−2046(3)	51(3)	46(3)	40(3)	−3(2)	8(2)	1(2)
C(2)	3775(4)	4071(4)	−2411(2)	57(3)	47(3)	38(2)	−10(2)	7(2)	0(2)
C(3)	4061(4)	3932(4)	−3172(2)	61(3)	51(3)	35(2)	−17(2)	12(2)	2(3)
H(2)	3808	3334	−3506	61	51	35	−17	12	2
C(4)	4861(4)	4721(5)	−3282(3)	66(3)	76(3)	54(3)	−10(3)	14(2)	13(3)
H(3)	5081	4757	−3852	66	76	54	−10	14	13
C(5)	5167(5)	5446(5)	−2644(4)	65(3)	71(3)	77(4)	−29(3)	15(3)	7(3)
H(4)	5720	6050	−2522	65	71	77	−29	15	7
S	4509(1)	5172(1)	1887(1)	88(1)	80(1)	62(1)	−41.5(7)	23.3(7)	−21.7(7)
O(2)	1442(3)	1834(3)	−1495(2)	63(2)	65(2)	38(2)	−26(1)	8(1)	−5(1)
C(6)	1585(4)	1915(4)	−2230(2)	54(2)	57(3)	32(2)	−13(2)	7(2)	−6(2)
C(7)	2286(4)	2594(4)	−2529(2)	58(3)	58(3)	32(2)	−12(3)	10(2)	−3(2)
H(1)	2340	2432	−3104	58	58	32	−12	10	−3
C(8)	831(5)	1110(5)	−2787(3)	70(4)	75(4)	46(4)	−35(3)	10(2)	−3(3)
F(1)	918(4)	1177(4)	−3532(2)	136(3)	152(3)	40(3)	−87(3)	20(2)	−25(2)
F(2)	−210(3)	1370(5)	−2781(2)	75(2)	195(5)	92(3)	−52(3)	6(3)	−44(3)
F(3)	905(5)	45(4)	−2554(3)	229(6)	80(3)	92(3)	−69(3)	−46(3)	1(2)
N	7717(3)	2815(3)	4589(2)	55(2)	43(2)	69(3)	7(2)	17(2)	0(2)
C(9)	6604(5)	2849(5)	4790(5)	72(4)	63(3)	125(6)	5(3)	43(3)	18(3)
H(5)	6658	3552	5142	72	63	125	5	43	18
H(6)	6058	2933	4182	72	63	125	5	43	18
C(10)	7847(5)	3972(5)	4182(4)	68(4)	54(3)	91(4)	9(3)	25(3)	13(3)
H(7)	7205	4099	3730	68	54	91	9	25	13
H(8)	7646	4617	4598	68	54	91	9	25	13
C(11)	7835(5)	1785(5)	4044(4)	82(4)	62(3)	94(4)	3(4)	9(3)	−20(3)
H(9)	8711	1780	3993	82	62	94	3	9	−20
H(10)	7720	1007	4406	82	62	94	3	9	−20
C(12)	8627(5)	2670(5)	5314(3)	97(4)	61(3)	71(3)	7(3)	1(5)	−1(3)
H(11)	8486	1952	5509	97	61	71	7	1	−1
H(12)	9359	2781	5016	97	61	71	7	1	−1
C(13)	6322(8)	1779(8)	5261(7)	132(7)	88(5)	205(10)	3(5)	94(7)	45(6)
C(14)	8919(6)	4129(7)	3895(5)	94(5)	95(5)	138(6)	−5(4)	56(5)	18(4)
C(15)	7076(9)	1828(9)	3226(6)	171(8)	132(7)	108(6)	2(5)	−24(6)	−54(6)
C(16)	8633(9)	3618(8)	5953(5)	181(9)	94(5)	86(5)	2(4)	−4(4)	−18(4)

TABLE II. Interatomic Distances (Å).[a]

Nb–O	1.704(3)	C(2)–S	1.700(5)
Nb–O(1)	2.285(3)	C(6)–C(8)	1.511(7)
Nb–O(2)	2.044(3)	C(8)–F(1)	1.290(6)
Nb–Cl(1)	2.365(2)	C(8)–F(2)	1.336(8)
Nb–Cl(2)	2.367(1)	C(8)–F(3)	1.273(8)
Nb–Cl(3)	2.422(2)		
O(1)–C(1)	1.246(6)		
O(2)–C(6)	1.295(6)	N–C(9)	1.494(8)
C(1)–C(7)	1.438(7)	N–C(10)	1.513(7)
C(6)–C(7)	1.338(5)	N–C(11)	1.513(8)
C(1)–C(2)	1.447(7)	N–C(12)	1.518(7)
C(2)–C(3)	1.411(7)	C(9)–C(13)	1.54(1)
C(3)–C(4)	1.383(7)	C(10)–C(14)	1.52(1)
C(4)–C(5)	1.356(8)	C(11)–C(15)	1.52(1)
C(5)–S	1.679(6)	C(12)–C(16)	1.53(1)

[a] Numbers in parentheses here and elsewhere indicate estimated standard deviations in the least significant digit(s).

Solution and Refinement of the Structure

Computations were performed using standard programs [3]; all calculations were carried out on the CII IRIS 80 System. For structure factor calculations the scattering factors were taken from Cromer and

TABLE III. Bond Angles (°)

O–Nb–Cl(1)	98.6(1)	O(1)–C(1)–C(2)	118.5(4)
O–Nb–Cl(2)	99.8(1)	C(7)–C(1)–C(2)	119.3(4)
O–Nb–Cl(3)	96.2(1)	C(1)–C(2)–C(3)	129.5(4)
O–Nb–O(1)	173.2(1)	C(1)–C(2)–S	119.8(3)
O–Nb–O(2)	94.8(1)	C(2)–C(3)–C(4)	111.5(5)
O(1)–Nb–O(2)	78.7(1)	C(3)–C(4)–C(5)	112.9(5)
Cl(1)–Nb–Cl(2)	90.7(1)	C(4)–C(5)–S	113.0(4)
Cl(1)–Nb–O(1)	83.5(1)	C(5)–S–C(2)	91.9(3)
Cl(1)–Nb–O(2)	89.7(1)	C(7)–C(6)–C(8)	119.4(4)
Cl(1)–Nb–Cl(3)	165.0(1)	O(2)–C(6)–C(8)	111.9(4)
Cl(2)–Nb–O(1)	86.6(1)	C(6)–C(8)–F(1)	114.5(4)
Cl(2)–Nb–O(2)	165.2(1)	C(6)–C(8)–F(2)	110.6(5)
Cl(2)–Nb–Cl(3)	89.3(1)	C(6)–C(8)–F(3)	112.7(5)
Cl(3)–Nb–O(1)	81.5(1)	F(1)–C(8)–F(2)	104.9(5)
Cl(3)–Nb–O(2)	86.6(1)	F(1)–C(8)–F(3)	110.3(5)
Nb–O(1)–C(1)	132.2(3)	F(2)–C(8)–F(3)	102.9(5)
Nb–O(2)–C(6)	134.6(3)		
O(1)–C(1)–C(7)	122.2(4)		
O(2)–C(6)–C(7)	128.7(4)		
C(1)–C(7)–C(6)	122.9(1)		
C(9)–N–C(10)	105.4(4)		
C(9)–N–C(11)	111.2(5)		
C(9)–N–C(12)	114.0(5)		
C(10)–N–C(11)	111.2(4)		
C(10)–N–C(12)	109.6(4)		
C(11)–N–C(12)	105.4(4)		
N–C(9)–C(13)	114.3(5)		
N–C(10)–C(14)	115.2(5)		
N–C(11)–C(15)	114.5(6)		
N–C(12)–C(16)	113.5(6)		

TABLE IV. Principal Values of rms Displacement (Å) and Volume of Ellipsoids (Å^3).

TABLE IV. *(continued)*

	Axes	rms	Volume
Nb	1	0.1661(6)	0.0304
	2	0.2021(10)	
	3	0.2165(7)	
Cl(1)	1	0.191(2)	0.0691
	2	0.288(2)	
	3	0.299(2)	
Cl(2)	1	0.179(1)	0.0450
	2	0.227(2)	
	3	0.264(2)	
Cl(3)	1	0.190(2)	0.0593
	2	0.270(2)	
	3	0.276(2)	
O	1	0.210(4)	0.0561
	2	0.248(4)	
	3	0.257(4)	
O(1)	1	0.169(5)	0.0453
	2	0.210(4)	
	3	0.306(4)	
O(2)	1	0.187(4)	0.0480
	2	0.204(4)	
	3	0.300(4)	
C(1)	1	0.198(7)	0.0400
	2	0.210(6)	
	3	0.229(6)	
C(2)	1	0.193(6)	0.0415
	2	0.203(6)	
	3	0.253(6)	
C(3)	1	0.178(6)	0.0410
	2	0.202(6)	
	3	0.272(6)	
C(4)	1	0.209(7)	0.0657
	2	0.254(7)	
	3	0.296(7)	
C(5)	1	0.190(7)	0.0695
	2	0.277(6)	
	3	0.315(7)	
S	1	0.200(2)	0.0724
	2	0.240(2)	
	3	0.359(2)	
C(7)	1	0.177(6)	0.419
	2	0.215(7)	
	3	0.263(6)	
C(6)	1	0.175(7)	0.0403
	2	0.210(7)	
	3	0.263(6)	
C(8)	1	0.195(7)	0.0575
	2	0.215(7)	
	3	0.328(7)	
F(1)	1	0.185(4)	0.0923
	2	0.247(4)	
	3	0.481(5)	
F(2)	1	0.216(5)	0.1325
	2	0.311(4)	
	3	0.470(6)	
F(3)	1	0.208(4)	0.1402
	2	0.292(5)	
	3	0.550(7)	
N	1	0.199(5)	0.0520
	2	0.236(5)	
	3	0.265(4)	

(continued overleaf)

TABLE IV. *(continued)*

	Axes	rms	Volume
	1	0.233(7)	
C(9)	2	0.248(7)	0.0886
	3	0.367(8)	
	1	0.221(7)	
C(10)	2	0.249(6)	0.0723
	3	0.313(7)	
	1	0.228(7)	
C(11)	2	0.283(7)	0.0889
	3	0.329(7)	
	1	0.244(7)	
C(12)	2	0.258(6)	0.0872
	3	0.330(7)	
	1	0.238(9)	
C(13)	2	0.322(9)	0.1573
	3	0.49(1)	
	1	0.247(8)	
C(14)	2	0.314(8)	0.1276
	3	0.392(9)	
	1	0.241(9)	
C(15)	2	0.38(1)	0.1839
	3	0.47(1)	
	1	0.264(8)	
C(16)	2	0.324(9)	0.1594
	3	0.44(1)	

TABLE V. Least-squares Planes. In the equations, x, y and z, represent fractional coordinates with respect to the crystallographic axes. The table gives the displacement (Å) of the specified atom from the plane.

Plane 1: square plane Cl(1), Cl(2), Cl(3) and O(2)
$-0.6022x -0.5275y +0.5993z + 3.9872 = 0$

Nb	0.295	O(1)	−1.987
O	1.999		

Plane 2: chelate ring, Nb, O(1), O(2), C(1), C(7) and C(6)
$0.6780x -0.7129y +0.1790z +0.3858 = 0$

Nb	0.0644	C(1)	0.0051
O(1)	−0.0673	C(7)	0.0169
O(2)	−0.0002	C(6)	0.0001

Plane 3: thenoyl ring C(2), C(3), C(4), C(5) and S
$0.6469x -0.6570y + 0.3870z + 1.0468 = 0$

C(2)	−0.0036	C(5)	−0.0106
C(3)	−0.0075	S	−0.0042
C(4)	−0.0005		

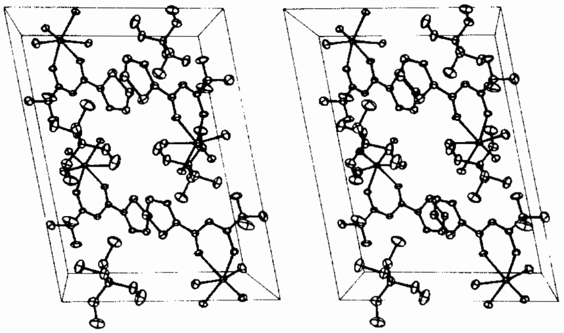


Figure 1. Stereo pair showing the unit cell. H atoms were omitted for clarity.

Waber's tabulation for all atoms [4]. The scattering factors for niobium and chlorine were corrected for the real and imaginary part of the anomalous dispersion, using the dispersion factors given by Cromer [5]. The agreement factors are defined in the usual way as $R = \Sigma(|F_{obs} - F_{calc}|)/\Sigma F_{obs}$ and $R_w = |\Sigma(w|F_{obs} - F_{calc}|)^2/\Sigma(wF_{obs})^2|^{1/2}$. In all least squares refinements, the quantity minimized was $\Sigma(w|F_{obs} - F_{calc}|)^2$. A weighting scheme based on counting statistics, $w = 2F/\sigma$, was employed for calculating R_w and in least-squares refinement.

Structure was solved by heavy atom techniques. Nb and Cl atoms were found from Patterson function. The subsequent Nb–Cl phased F_{obs} synthesis indicated C, O, F and S atoms. A difference Fourier synthesis revealed C and N atoms of the cation $(C_2H_5)_4N$. Atomic positions were refined by full matrix least-squares with isotropic temperature factors; two cycles of refinement gave convergence at R 0.16. When these atoms were refined anisotropically R dropped to 0.046 after three cycles. At this stage 25 reflexions with large discrepancy ($F_{obs} - F_{calc}$) which could be related to errors in manual setting, were excluded from the refinement. The introduction of an isotropic secondary extinction correction [6] led to R 0.042, with an extinction parameter of 2.7×10^{-7}; Hamilton's test indicated this decrease to be significant [7].

Positions of H atoms related to the anion and those of the CH_2 groups of the cation were calculated and introduced in the last two cycles of refinement. H temperature factors were constrained to be the same as those of the C atoms to which these H atoms were bound. Convergence was then reached at R 0.040 and R_w 0.037 (2409 observations, 254 variables).

Atomic coordinates and anisotropic components U_{ij} of temperature factors are shown in Table I; bond lengths and angles, with estimated standard deviations in Table II and III. R.m.s. displacements for all atoms but H are given in Table IV. Details of important molecular planes are in Table V. The observed structure amplitudes and structure factors

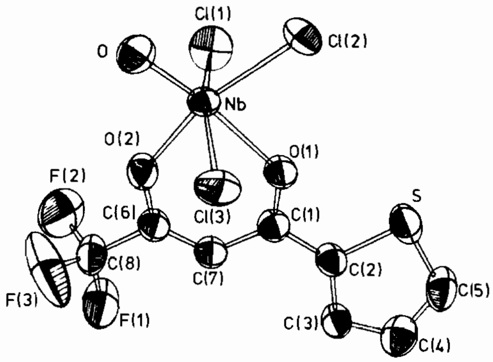


Figure 2. An ORTEP drawing of the anion.

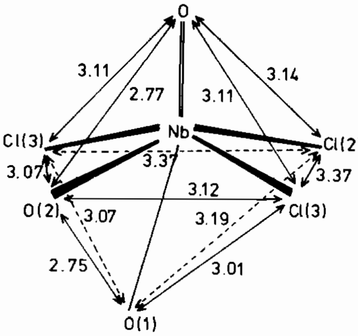


Figure 3. Close Cl–Cl and Cl–O contacts (Å).

calculated from the parameters of Table I are available from the Editor; F(000) is 1082.

Discussion

The crystal is built up of isolated tetraethylammonium cations and trichlorooxo(trifluorothenoylbutanedionato)niobate(V) anions (Figure 1). The nitrogen and niobium atoms are at general positions in the unit cell. Within experimental errors the dimensions of the tetraethylammonium cations agree with those of previous determinations [8, 9]. A view of the anion is shown in Figure 2. The niobium atom is at the centre of a distorted coordination octahedron of three chlorine atoms, the chelating diketone and the oxo oxygen atom. The niobium–oxygen bond, 1.704 Å, is within experimental error the same as those in the oxopentathiocyanatoniobate(V) [10], oxotrioxalatoniobate [11] and diacetonitriletrichloromonooxoniobium(V) [12] complexes. The bond length is consistent with a Nb–O multiple bond. A bond order of two was suggested by Wendling and Röhmer [13].

The niobium atom is displaced by 0.295 Å out of the Cl(1), Cl(2), Cl(3) and O(2) plane towards the oxo oxygen atom. The overall stereochemistry resembles that found in other oxo-niobium or vanadium systems; the Nb–Cl lengths, 2.365, 2.367 and 2.422 Å, are of the same order as those found in the above oxo complexes. However, of the two Nb–Cl bonds *trans* to one another, Nb–Cl(3), 2.422 Å, is significantly longer than Nb–Cl(2), 2.367 Å. It may be argued on the basis of close Cl–Cl and Cl–O contacts (Figure 3), that the lengthening is related to steric repulsions rather than *trans*-effect which should increase both the Nb–Cl distances by the same extent.

The O(1), C(1), C(7), C(6) and O(2) atoms form a six membered chelate ring at the Nb with O(1)–Nb–O(2) angle equal to 78.7(1)°. The calculation of the best planes through the chelate ring showed it to be planar (Table V) within experimental error. This structure determination shows that the oxygen atom of the ketone group nearest to the thenoyl ring is in *trans* position with respect to the oxo oxygen atom O; thus the isomer (a) occurs in the solid state. Of the two niobium–oxygen distances 2.044(3) and 2.285(3) Å, Nb–O(1) length in *trans* with respect to the oxo oxygen atom is considerably longer. This is comparable to the lengthening of the niobium–nitrogen bond *trans* to the multiple bond system Nb=O in the $NbOCl_3(CH_3CN)_2$ complex [12]; the difference in length was suggested to be related to the valence shell electron pair repulsions between Cl and O atoms.

Within experimental errors, dimensions in the thenoyltrifluorobutanedionato (TTA) agree fairly well with the observed values in $Rh(TTA)(CO)(PPh_3)$ [14] and $Nd(TTA)_3 \cdot 2TPPO$ [15]. The thenoyl ring is planar (Table V) and makes an angle of 12.8° with the chelate ring. As in the above complexes the sulphur oxygen distance of 2.918 Å is significantly shorter than the sum of the van der Waals radii of sulphur and oxygen, 3.25 Å [16].

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