Short Communications

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Acta Cryst. (1970). B**26**, 872

The crystal and molecular structure of bis(tetramethylurea)dichloro-oxovanadium(IV).

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(*Received* 19 *December* 1969)

Bis(tetramethylurea)dichloro-oxovanadium(IV), $VOCl_2(C_5H_{12}N_2O)_2$, crystallizes in a monoclinic lattice, space group $C2/c$ ($Z=4$) with cell dimensions $a=18{\cdot}57\pm0{\cdot}02$, $b=7{\cdot}87\pm0{\cdot}01$, $c=13{\cdot}34\pm0{\cdot}01$ Å; $\beta=113{\cdot}5\pm0{\cdot}4°$. The crystal structure has been determined by three-dimensional Patterson and Fourier techniques. Refinement of the atomic parameters employing the full-matrix least-squares method led to a final R index of 0·099. The vanadium atom is pentacoordinated with the following metal-to-ligand bond lengths: V–Cl, $2{\cdot}340\pm0{\cdot}005$; V=O, $1{\cdot}61\pm0{\cdot}03$ and V–O, $2{\cdot}00\pm0{\cdot}02$ Å.

Oxovanadium(IV) is known to form five-coordinated complexes with the V=O bond essentially a double bond (Selbin & Holmes, 1962). The compound bis(tetramethylurea)-dichloro-oxovanadium(IV), $VOCl_2(C_5H_{12}N_2O)_2$, displays pentacoordination of the square pyramidal type.

The dark blue crystals of $VOCl_2(C_5H_{12}N_2O)_2$ are monoclinic with space group $C2/c$ (systematic absences: hkl for $h+k\neq2n$, $h0l$ for $l\neq n$). Measurements made on oscillation, Weissenberg and precession photographs gave the following unit-cell dimensions:

$$a=18{\cdot}57\pm0{\cdot}02,\ b=7{\cdot}87\pm0{\cdot}01,\ c=13{\cdot}34\pm0{\cdot}01\ \text{Å},$$
$$\beta=113{\cdot}5\pm0{\cdot}4°.$$

The crystal density measured by flotation is 1·40 g.cm^{-3} while the calculated density based on 4 molecules per unit cell is 1·38 g.cm^{-3}. A total of 558 independent reflexions were recorded with rotation about the b axis ($k=0$ to 4) using the multiple-film, equi-inclination Weissenberg technique with Cu $K\alpha$ radiation. A calibrated strip was used for the intensity measurements. Since the crystal shape was spherical (diameter ~0·25 mm) absorption corrections were made according to *International Tables for X-ray Crystallography* (1962). The standard Lorentz and polarization corrections were applied.

With the space group $C2/c$ having eight general positions and there being four molecules of $VOCl_2(C_5H_{12}N_2O)_2$ in the unit cell, the four V=O groups are required to lie on twofold axes. The trial structure followed from three-dimensional Patterson and Fourier syntheses. Refinement of the atomic parameters was carried out using a full-matrix least-squares program (Busing, Martin & Levy, 1962). By including only the observed reflexions (Dunning & Vand, 1969) in the refinement with equal weighting and isotropic thermal parameters for all the atoms, the final R index ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was reduced to 0·099. Table 1 lists the refined atomic parameters. Interatomic distances and bond angles were calculated with the aid of the program *ORFFE* (Busing, Martin & Levy, 1964). These quantities are summarized in Table 2. The observed and calculated structure factors are given in Table 3.

Fig. 1 shows a view of the molecule and the atomic numbering used. The square pyramidal arrangement of the ligands about the central vanadium atom involves the two chlorine and two oxygen atoms at the base and the third oxygen atom at the apex. The least-squares plane through the four atoms forming the base of the square pyramid is given by the equation

$$0{\cdot}01855\,X+0{\cdot}9996\,Y-0{\cdot}02\ 173\,Z=1{\cdot}9552^*$$

and shows them to be coplanar to within ±0·015 Å. Good agreement exists between the bond lengths obtained for the

* X, Y and Z are the orthogonalized axes with X in the direction of **a** and Y in the plane of **a** and **b**.

Table 1. *Refined atomic parameters (fractional coordinates and isotropic temperature factors)*

Standard deviations are given in parentheses.

V	0·00	0·1862 (8)	0·25	4·77 (12)
Cl	0·1280 (2)	0·2668 (8)	0·2783 (4)	5·83 (14)
O(1)	0·00	−0·0188 (4)	0·25	8·24 (62)
O(2)	0·0287 (6)	0·2501 (17)	0·4063 (8)	5·72 (30)
N(1)	0·1311 (8)	0·2045 (27)	0·5702 (12)	7·27 (42)
N(2)	0·1055 (8)	0·4762 (26)	0·4878 (11)	6·06 (39)
C(1)	0·0886 (9)	0·3132 (32)	0·4856 (13)	5·13 (42)
C(2)	0·1236 (13)	0·0183 (39)	0·5547 (18)	9·34 (70)
C(3)	0·1661 (10)	0·2678 (30)	0·6878 (15)	7·35 (54)
C(4)	0·0496 (10)	0·5988 (30)	0·4085 (14)	6·67 (52)
C(5)	0·1890 (10)	0·5378 (31)	0·5430 (14)	7·37 (56)

V=O and V–O distances, *viz.* 1·61 ± 0·03 and 2·00 ± 0·02 Å respectively, and the corresponding literature values, *viz.* (1·56–1·65) ± 0·03 and 1·97 ± 0·01 Å respectively (Selbin, 1965; Dodge, Templeton & Zalkin, 1961). The bond length for V–Cl is 2·340 ± 0·005 Å. This value is significantly larger than the V–Cl lengths in $VCl_3[N(CH_3)_3]$ of 2·241 ± 0·004 and 2·236 ± 0·005 Å reported by Greene & Orioli (1969) and that in $VOCl_2[N(CH_3)_3]$ of 2·250 ± 0·005 Å of Drake, Vekris & Wood (1968). In these two molecules, however, we find an example of trigonal bipyramidal hybridization of the vanadium atom with the chlorine atoms bonded to the somewhat shorter equatorial hybrid orbitals compared with the four equivalent basal orbitals of the square pyramid.

The least-squares plane through C(1), O(2), N(1) and N(2) is given by

$$0{\cdot}8539\,X - 0{\cdot}2101\,Y - 0{\cdot}4761\,Z = -4{\cdot}1644$$

and indicates these atoms to be planar to within ± 0·018 Å. Slightly twisted out of this plane are the four methyl carbon atoms C(2), C(3), C(4) and C(5), which show perpendicular ceviations of 0·34, −0·77, −0·27 and 0·64 Å respectively.

The closest approach of two vanadium atoms is 7·28 Å and these are in molecules which are related by a centre of symmetry. The shortest intermolecular contact distance of 3·58 Å is of the van der Waals type and occurs between C(4) and O(1) where the latter atom is in the molecule related to the parent molecule by a unit-cell translation in the **b** direction.

This analysis was undertaken at the request of Professor J. G. H. du Preez of the University of Port Elizabeth, who also provided the crystals.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program.* ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Standard deviations are given in parentheses.

Bond	Distance	Bond	Distance
V–Cl	2·340 (5) Å	C(1)–N(1)	1·38 (3) Å
V–O(1)	1·61 (3)	C(1)–N(2)	1·32 (3)
V–O(2)	2·00 (2)		
		N(1)–C(2)	1·48 (3)
Cl ···Cl′	4·505 (9)	N(1)–C(3)	1·52 (3)
O(2)···O(2′)	3·87 (2)		
		N(2)–C(4)	1·50 (2)
C(1)–O(2)	1·29 (2)	N(2)–C(5)	1·51 (2)
Bond	**Angle**	**Bond**	**Angle**
Cl—V–Cl′	148·6 (3)°	N(1)–C(1)–N(2)	122·0 (1·8)°
O(1)–V–O(2)	104·6 (4)		
O(2)–V–O(2)	150·7 (5)	C(1)–N(1)–C(2)	120·4 (1·9)
O(1)–V–Cl	105·7 (2)	C(1)–N(1)–C(3)	120·5 (2·0)
O(2)–V–Cl	86·1 (4)	C(1)–N(2)–C(4)	121·2 (1·6)
		C(1)–N(2)–C(5)	120·9 (1·7)
C(1)–O(2)–V	137·4 (1·0)		
		C(2)–N(1)–C(3)	116·5 (1·8)
O(2)–C(1)–N(1)	117·1 (2·1)	C(3)–N(2)–C(4)	115·2 (1·7)
O(2)–C(1)–N(2)	120·8 (1·8)		

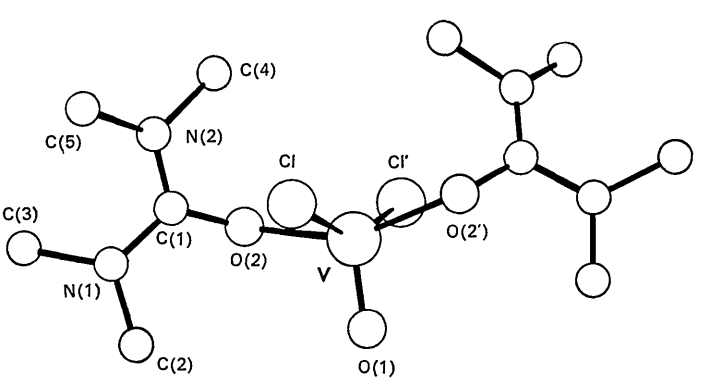

Fig. 1. Molecular geometry and atomic numbering.

Table 3. *Observed and calculated structure factors*

The columns are h, l, $F_{obs} \times 10$ and $F_{calc} \times 10$.

	K = 0		
C	2	261	-273
0	4	2002	1883
0	6	1303	-1230
0	8	386	353
0	12	252	193
2	0	1633	1815
2	2	662	-553
2	4	184	-161
2	6	687	-632
2	8	235	123
2	10	365	330
2	12	241	229
4	0	1241	-1185
4	2	485	277
4	6	374	-340
4	8	379	313
4	10	257	-238
4	12	312	291
6	0	1029	1081
6	2	742	-749
6	4	1031	1088
6	6	980	-1039
6	8	105	120
6	10	426	-483
6	12	147	150
8	0	1372	1505
8	2	785	-761
8	4	947	924
8	6	650	-642
-2	2	384	-493
-2	4	1277	1322
-2	6	1323	-1286
-2	8	1286	1203
-2	10	729	-638
-2	12	364	363
-2	14	309	-328
-4	2	2143	-2004
-4	4	1432	-1319
-4	6	1221	-1058
-4	8	676	570
-4	10	344	-319
-4	12	149	164
-4	14	398	-380
-6	2	1993	-2114
-6	4	962	-905
-6	6	312	-291
-6	10	343	242
-6	12	149	-10
-6	14	161	-127
-8	2	1453	-1444
-8	4	1084	1084
-8	6	686	-685
-8	8	977	997
-8	10	245	-226
-8	12	211	229
10	0	537	509
10	2	227	160
10	4	248	261
12	0	191	-183
12	4	211	258
14	0	146	133
14	2	395	-401
14	4	430	436
14	6	212	-208
16	0	363	359
16	2	282	-327
16	4	123	140
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-10	4	1454	1612
-10	6	363	-370
-10	8	1241	1210
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-10	14	271	-265
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-14	10	149	-168
-16	2	448	-466
-16	4	515	612
-16	6	471	-534
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-16	10	360	-384
-18	2	143	-168
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-18	8	353	356
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-18	12	245	252
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1	4	110	24
1	5	277	-285
1	6	549	-515
1	7	184	148
1	9	173	-79
1	10	255	-265
3	0	609	699
3	1	276	400
3	2	1057	-990
3	3	292	-319
3	4	325	242
3	5	135	168
3	6	331	-319
3	8	171	189
3	9	179	181
3	10	162	-160
3	11	175	140
5	0	300	472
5	1	339	-331
5	2	570	-459
5	3	126	147
5	4	552	500
5	5	635	-647
5	7	727	695
5	8	358	323
5	9	128	-196
5	11	283	315
7	0	720	800
7	1	1104	-1089
7	2	190	148
7	3	611	671
7	4	377	395
7	5	697	-711
7	7	476	495
7	8	181	182
7	9	249	-230
9	0	312	351
9	1	437	-527
9	2	375	-412
9	3	279	288
9	5	249	-343
9	6	256	-313
9	7	181	-123
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-1	3	1778	1534
-1	4	469	332
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-1	7	1294	1140
-1	9	671	-610
-1	10	307	-262
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-3	3	540	-540
-3	4	1612	1491
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-3	6	309	294
-3	7	721	703
-3	8	401	409
-3	9	400	-367
-3	10	123	-84
-3	11	442	405
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-5	2	537	-425
-5	3	1080	-1026
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-5	6	180	-138
-5	8	603	549
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-5	12	314	357
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-7	11	179	-135
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11	1	231	216
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11	3	175	-159
11	5	181	-182
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2	8	151	136
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4	5	745	-677
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6	2	225	270
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6	8	179	-260
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1	6	393	345
1	8	294	-266
1	9	177	-150
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3	3	907	859
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3	7	238	233
3	8	304	-289
3	9	252	-218
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5	4	365	-334
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5	6	292	196
5	7	351	-331
7	0	265	-262
7	3	557	-518
7	5	452	479
7	6	125	143
7	7	218	-203
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0	6	274	-215
0	7	168	-147
0	9	256	253
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2	1	493	526
2	3	678	-616
2	4	286	-326
2	5	537	497
2	7	428	-368
2	9	313	273
2	10	174	226
2	11	160	-184
4	0	498	-621
4	1	672	694
4	2	233	353
4	3	523	-422
4	4	269	-340
4	5	439	384
4	7	312	-230
4	9	176	184
6	0	274	290
6	1	574	608
6	2	151	-147
6	3	160	-147
6	4	238	229
6	5	248	144
6	6	313	-306
8	0	538	548
8	1	160	113
8	2	129	-143
8	3	300	-273
8	4	252	241
8	5	140	105
8	6	180	-174
8	7	174	-176
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-2	3	490	-494
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-2	7	284	-257
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-2	9	161	103
-2	10	256	-216
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-4	2	200	59
-4	3	573	-582
-4	4	473	-526
-4	5	617	658
-4	6	215	-85
-4	7	430	-398
-4	9	178	156
-4	11	178	-212
-6	1	230	257
-6	2	265	-174
-6	3	467	-541
-6	4	420	-435
-6	5	590	612
-6	7	285	-264
-6	8	172	-242
-6	9	309	383
-6	10	256	286
-6	11	179	-218
-8	1	214	196
-8	2	299	-305
-8	3	212	-163
-8	4	215	213
-8	5	222	181
-8	6	230	-211
-8	7	239	-243
-8	8	248	218
-8	9	254	240
10	1	174	189
10	2	309	292
10	3	362	-267
10	5	251	222
12	0	312	-235
12	1	363	352
12	2	162	153
12	3	178	-181
-10	1	503	493
-10	4	287	275
-10	5	291	341
-10	6	171	-193
-10	7	175	-177
-10	8	310	373
-12	1	310	352
-12	3	353	-346
-12	4	250	-274
-12	5	307	323
-12	6	253	246
-12	7	255	-284
-14	2	140	-147
-14	3	314	-280
-14	4	257	-237
-14	5	140	139
-14	7	313	-328
-16	2	172	-186
-16	4	175	202

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