1096. *The Crystal Structure of Diammonium Oxotetrakisisothiocyanatovanadate Pentahydrate.*

By A. C. Hazell.

A three-dimensional *X*-ray crystal-structure analysis of the complex $(NH_4)_2VO(NCS)_4,5H_2O$ has shown the vanadium atom to be co-ordinated to the vanadyl-oxygen atom and to the four nitrogen atoms of the isothiocyanate groups, these five atoms are arranged at the vertices of a tetragonal pyramid, there is a close approach to a water molecule in the remaining "octahedral" position; the complex anion has the symmetry $4m = C_v^4$ within experimental error. The bond lengths and angles are compared with those in other vanadyl and other isothiocyanate compounds.

QUADRIVALENT vanadium readily forms complexes in which the vanadyl ion $[VO]^{2+}$ is linked to four other groups. The thiocyanate complexes $M_2VO(NCS)_4,5H_2O$ (where $M = K$ or NH_4) have been studied by *X*-ray diffraction to determine whether the vanadium is, in fact, five-co-ordinated as its formula suggests, and if so whether it adopts the square-pyramidal or the trigonal-bipyramidal configuration; and also to determine whether the SCN group co-ordinates as the thiocyanate or the isothiocyanate.

Crystal Data.—$(NH_4)_2VO(NCS)_4,5H_2O$, $M = 425{\cdot}4$. Monoclinic, $a = 16{\cdot}50 \pm 0{\cdot}05$, $b = 6{\cdot}82 \pm 0{\cdot}02$, $c = 16{\cdot}32 \pm 0{\cdot}05$ Å, $\beta = 94{\cdot}5 \pm 0{\cdot}5°$. $U = 1821$ Å^3, $D_m = 1{\cdot}52$ (by flotation), $Z = 4$, $D_c = 1{\cdot}55$, $F(000) = 876$. Space-group, $P2_1/n$ (C_{2h}^5, No. 14). Single-crystal oscillation and Weissenberg photographs. Cu-K_α radiation, absorption coefficient $\mu = 92$ cm.$^{-1}$.

$K_2VO(NCS)_4,5H_2O$, $M = 467{\cdot}6$. Monoclinic, $a = 16{\cdot}30 \pm 0{\cdot}05$, $b = 6{\cdot}80 \pm 0{\cdot}02$, $c = 16{\cdot}30$ Å, $\beta = 94{\cdot}5 \pm 0{\cdot}5°$. $U = 1801$. $D_m = 1{\cdot}82$ (by flotation), $Z = 4$, $D_c = 1{\cdot}73$. $F(000) = 940$. Space-group $P2_1/c$ (C_{2h}^5, No. 14). Single-crystal oscillation and Weissenberg photographs, CuK_α radiation.

The salts are not isomorphous. Both form deep-blue needle-shaped crystals which are elongated in the [010] direction and are strongly pleochroic, the deepest colour when viewed in polarised light being exhibited when the [010] axis is perpendicular to the vibration direction of the magnetic vector; this suggests that the V–O groups are roughly parallel to the *b*-axis.

Structure Determination.—A three-dimensional sharpened Patterson function showed the vanadium atom to be situated close to $\frac{1}{4},\frac{1}{4},0$, but failed to yield any other information; as the vanadium atom gave only the phases of reflections with indices h,k,l all even, or all odd, an electron-density map calculated by using the phases from the vanadium atom gave no further information. There were insufficient large unitary structure factors for inequality methods to be applied successfully.

The $h0l$ projection was eventually solved by comparing the structure factors observed with Cu-K_α ($\lambda = 1{\cdot}542$ Å) and Cr-K_α ($\lambda = 2{\cdot}291$ Å) radiation. As the wavelength of Cr-K_α radiation is close to the *K* absorption edge for vanadium (2·269 Å), the atomic scattering factor for vanadium must be replaced by $f = f_0 + \Delta f + i\Delta f''$, where f_0 is the usual value for the atomic

TABLE 1.

Observed and calculated structure factors (reflections which are too weak to be observed have been omitted).

l	$\lvert F_o \rvert$	F_c
	0 0 *l*	
2	66	75
4	76	67
6	167	−153
8	55	38
10	30	−20
12	71	74
14	52	−46
16	17	2
18	16	−15
20	21	14
	1 0 *l*	
3	27	−30
5	52	−44
7	18	−15
9	45	−33
11	59	−41
13	13	−16
17	22	−31
19	29	−31
	2 0 *l*	
0	92	−111
2	37	−19
4	262	−261
6	75	−82
8	80	−74
10	31	34
14	20	19
	3 0 *l*	
1	13	5
3	103	104
5	8	−3
7	74	78
11	41	33
13	29	36
15	46	56
17	17	19
19	18	15
	4 0 *l*	
0	111	105
2	123	91
4	100	−111
6	26	22
8	25	−20
10	85	108
14	27	18
16	13	−23
18	11	−1
20	19	−20
	5 0 *l*	
1	22	18
3	13	−7
5	34	−40
7	71	−70
9	34	−37
11	53	−62
15	22	−20
17	29	−32
19	18	−31
	6 0 *l*	
0	147	124
2	24	−20
4	64	61
6	115	−98
8	43	36
10	29	−28
12	54	53
14	22	−22
16	22	−8
18	16	−23
	7 0 *l*	
1	55	40
9	41	43
11	21	13
13	28	45
15	24	31
17	26	26
	8 0 *l*	
0	178	111
2	112	89
8	19	−25
10	30	37
12	15	−7
	9 0 *l*	
1	35	−49
5	44	−46
9	65	−60
11	15	−26
13	26	−36
	10 0 *l*	
0	41	−40
2	43	34
4	56	−51
8	44	−64
	11 0 *l*	
1	29	28
3	67	59
5	33	41
7	38	28
13	25	33
15	19	31
	12 0 *l*	
0	68	60
2	61	38
4	75	75
6	29	−26
10	17	−13
12	12	21
	13 0 *l*	
1	13	−11
3	28	−37
7	37	−36
9	13	−21
11	27	−42
15	9	−19
	14 0 *l*	
0	13	7
2	53	42
	15 0 *l*	
3	25	27
7	37	41
	16 0 *l*	
0	24	19
2	37	40
	17 0 *l*	
1	26	−22
	18 0 *l*	
0	21	−21
	−1 0 *l*	
1	25	23
7	17	−11
9	38	41
11	26	24
13	57	65
15	22	29
19	15	15
	−2 0 *l*	
2	47	−41
4	74	−77
6	15	14
8	29	−19
10	40	45
12	44	−43
16	22	−20
	−3 0 *l*	
3	17	−5
5	41	−44
7	40	−28
9	45	−48
11	30	−36
17	38	−39
	−4 0 *l*	
2	158	187
4	136	−120
6	86	95
8	45	41
10	73	74
12	13	11
16	19	−21
	−5 0 *l*	
1	25	7
3	19	32
7	35	34
11	20	21
13	47	41
15	17	24
17	13	18
	−6 0 *l*	
2	243	−315
4	140	−143
6	113	−109
8	35	37
10	12	−11
14	76	−80
18	11	−5
	−7 0 *l*	
5	29	−26
7	13	−10
9	21	−14
15	22	−28
17	30	−35
	−8 0 *l*	
2	135	113
4	37	39
6	64	61
8	40	44
10	87	65
16	25	−21
	−9 0 *l*	
1	25	−21
9	16	19
11	21	23
13	31	35
15	17	19
	−10 0 *l*	
2	137	−105
4	186	−155
6	12	5
8	26	12
14	22	−22
	−11 0 *l*	
7	36	−11
11	15	−16
15	19	−25
	−12 0 *l*	
2	69	−60
4	31	29
6	37	8
8	35	70
10	24	18
12	25	29
14	16	−14
	−13 0 *l*	
1	19	−17
11	19	20
13	12	16
	−14 0 *l*	
2	46	−19
4	136	−93
6	35	−29
8	37	−40
12	55	−44
	−15 0 *l*	
11	19	−4
	−16 0 *l*	
4	40	38
6	95	72
8	56	33
10	15	14
	−17 0 *l*	
1	27	−25
	−18 0 *l*	
2	53	−50
4	26	−5
6	31	−22
8	31	17
10	30	−24
	−20 0 *l*	
4	63	−11
6	46	38
	0 1 *l*	
2	11	−17
3	21	29
4	27	−22
6	93	−91
8	37	−35
9	20	18
13	26	25
14	26	−30
	1 1 *l*	
1	136	−157
2	13	−16
3	160	−177
4	25	−29
5	167	−166
6	92	−83
8	20	24
9	26	−7
10	47	−46
12	37	30
	2 1 *l*	
1	19	−26
2	27	28
3	17	−21
4	22	18
7	22	−25
8	65	59
9	30	−4
10	71	82
11	24	−27
12	38	41
	3 1 *l*	
0	52	−71
1	80	75
2	55	58
3	148	−119
4	26	27
6	80	76
7	85	93
8	59	−26
9	120	135
10	36	43
11	18	26
12	43	−44
14	24	24
15	24	−27
	4 1 *l*	
0	31	−29
1	30	26
3	12	−12
6	50	−57
7	20	25
8	46	−48
10	24	−20
11	27	26
12	34	−45
	5 1 *l*	
0	77	83
1	89	−63
2	91	−92
3	59	−55
4	37	−41
5	56	−52
6	31	−27
7	43	49
	6 1 *l*	
0	28	21
1	16	−17
2	50	38
4	48	47
6	19	−18
10	31	38
12	26	52
	7 1 *l*	
1	93	78
2	45	39
3	30	26
4	41	47
7	40	41
8	25	28
10	25	−27
13	24	−40
	8 1 *l*	
0	34	−24
4	38	−32
6	67	−64
8	41	−38
	9 1 *l*	
0	53	−60
1	44	31
3	103	−88
4	53	−58
5	63	−65
6	46	31
7	45	−46
8	25	−32
9	20	21
10	29	38
12	20	−24
	10 1 *l*	
2	41	30
4	46	47
6	21	29
8	26	23
10	29	39
	11 1 *l*	
0	52	57
1	53	50
3	18	17
4	27	25
5	19	−19
7	24	24
	12 1 *l*	
6	44	−44
	13 1 *l*	
2	28	−31
3	26	−24
5	45	−54
	14 1 *l*	
2	29	32
4	24	24
	15 1 *l*	
1	53	46
2	17	30
	17 1 *l*	
5	22	−27
	18 1 *l*	
3	21	−18
	−1 1 *l*	
1	71	76
2	27	−49
4	31	40
6	78	69
7	95	95
8	35	23
9	41	30
13	25	−29
14	26	−19
	−2 1 *l*	
1	13	−32
2	29	29
3	12	−19
4	25	24
5	16	−12
6	12	−12
7	31	35
8	17	24
9	27	−24
10	58	52
12	25	22
13	28	−28
14	26	30
	−3 1 *l*	
1	81	−70
2	43	89
3	151	−183
4	65	−76
7	36	30
8	82	−78
9	26	31
10	28	29
11	66	−68
12	47	−49
13	20	−29
14	33	35
	−4 1 *l*	
1	17	21
3	12	16
6	28	−34
7	13	−11
8	15	−6
10	17	−7
11	18	10
12	43	−45
14	40	−50
	−5 1 *l*	
1	47	46
2	68	−77
3	29	43
4	35	62
7	84	109
8	56	72
9	27	32
10	18	−27
11	18	16
12	38	41
14	17	−20
	−6 1 *l*	
1	28	−30
2	9	6
8	31	38
10	46	56
11	13	−26
12	27	31
	−7 1 *l*	
1	129	−108
3	90	−74
4	19	28
5	24	−35
6	22	−26
7	20	18
8	13	−13
10	21	−26
11	47	−72
13	33	−47
	−9 1 *l*	
1	19	27
2	57	66
3	21	23
4	62	−76
5	143	123
6	53	62
7	100	86
9	45	44
10	27	45

TABLE 1. (*Continued.*)

l	$\lvert F_o \rvert$	F_c
	−11 1 *l*	
1	118	−88
2	38	−43
3	71	−53
4	26	39
5	21	−24
7	50	37
10	26	−29
11	29	−17
13	37	−23
	−12 1 *l*	
2	19	19
3	15	26
	−13 1 *l*	
1	16	−16
2	25	−9
4	54	20
5	24	36
6	64	−22
8	17	20
10	26	−3
12	27	11
14	34	7
	−15 1 *l*	
1	26	−24
2	34	32
3	17	−35
5	24	−6
6	24	32
8	17	−25
10	53	8
	−17 1 *l*	
2	37	−19
4	57	17
6	46	−13
	0 2 *l*	
0	147	−107
1	50	−48
2	290	−217
3	93	88
4	71	68
5	34	−94
6	40	−31
7	21	18
9	87	−65
10	100	−72
11	25	16
13	44	−30
15	31	7
	1 2 *l*	
0	56	−39
1	30	22
2	54	−53
3	22	15
4	38	−33
5	44	38
6	45	−31
7	37	23
8	24	−20
9	56	31
11	53	43
13	45	10
17	31	19
	2 2 *l*	
0	242	−190
1	30	24
2	184	124
4	169	152
5	100	64
6	200	171
7	31	17
8	78	57
9	48	36
13	22	19
14	27	9
	3 2 *l*	
1	75	−50
2	98	70
3	55	−32
4	43	35
5	78	−56
6	34	31
7	20	−12
9	53	−34
10	34	26
13	50	−50
	4 2 *l*	
0	120	−97
1	35	64
2	20	−12
3	40	−36
4	52	−31
5	24	−12
6	31	12
7	81	−61
8	92	−64
10	33	−40
11	34	−26
12	54	−52
15	34	−27
	5 2 *l*	
0	19	−18
5	53	48
6	39	−29
7	39	31
8	27	−15
9	72	66
10	20	−12
11	46	26
	6 2 *l*	
1	67	−56
2	101	−59
3	110	78
4	124	85
5	28	−13
6	30	25
7	66	64
8	75	60
10	52	−55
11	38	31
15	33	32
	7 2 *l*	
0	36	29
2	21	18
3	62	−33
4	40	28
6	29	7
7	62	−46
8	20	19
	8 2 *l*	
0	175	−119
2	147	−89
3	46	−33
4	52	−36
7	38	−29
	9 2 *l*	
0	68	−54
1	36	20
3	22	18
4	24	−21
5	28	−7
7	45	31
8	27	−23
11	45	50
	10 2 *l*	
0	24	19
1	45	36
2	46	33
3	31	16
4	20	15
5	47	39
6	77	67
	14 2 *l*	
1	22	20
2	22	−21
	16 2 *l*	
1	30	−8
3	27	−16
5	25	−1
	18 2 *l*	
0	45	36
1	38	−2
	−1 2 *l*	
2	40	51
3	53	−40
4	43	45
5	29	21
7	38	−34
8	24	15
9	21	−14
11	54	−44
13	52	−45
15	36	−29
	−2 2 *l*	
1	46	58
2	56	−39
3	36	−45
4	48	58
5	18	23
6	49	42
8	28	20
10	56	22
13	35	31
14	39	30
	−3 2 *l*	
4	24	−27
5	35	33
6	34	−27
7	37	38
8	24	−22
9	65	47
11	35	34
	−4 2 *l*	
1	63	52
2	112	143
5	17	16
6	24	−21
7	49	−52
8	106	−100
10	82	−71
11	33	−37
	−5 2 *l*	
2	43	24
	−6 2 *l*	
1	24	−24
3	38	47
4	115	156
5	41	−54
6	55	45
7	50	56
8	26	28
11	40	46
12	49	42
	−7 2 *l*	
4	46	−44
	−8 2 *l*	
1	24	28
2	44	13
4	50	28
6	50	−44
8	53	−64
10	34	−45
12	33	−32
	−9 2 *l*	
1	55	43
2	43	26
4	57	32
	−10 2 *l*	
1	46	28
2	111	83
4	57	32
	−11 2 *l*	
6	26	−21
	−12 2 *l*	
2	44	15
4	112	69
5	27	−27
6	38	−25
7	35	23
8	53	−33
9	33	−28
10	62	−44
	−14 2 *l*	
2	82	50
4	41	23
6	36	26
7	27	−14
9	34	19
10	37	33
12	36	23
14	55	32
	−16 2 *l*	
4	58	−25
6	56	−32
	−18 2 *l*	
2	33	35
4	45	27
	0 3 *l*	
3	58	−54
4	36	42
5	71	−73
6	58	51
7	45	−45
8	28	22
	1 3 *l*	
3	234	166
4	22	−20
5	69	69
7	52	32
8	45	43
	2 3 *l*	
3	52	52
4	31	−34
5	56	65
	3 3 *l*	
1	93	61
3	39	−23
4	31	30
5	58	48
6	47	−33
7	136	−120
	4 3 *l*	
3	47	−40
6	45	31
7	26	−31
	5 3 *l*	
4	40	12
5	54	8
7	58	−18
	7 3 *l*	
1	135	−87
6	62	−41
	8 3 *l*	
2	40	26
3	43	−29
6	45	37
	9 3 *l*	
5	99	88
	12 3 *l*	
0	26	24
	−1 3 *l*	
1	13	−15
2	20	27
5	37	−42
7	29	−46
8	28	−35
	−2 3 *l*	
1	50	34
3	39	49
4	22	−31
5	31	38
7	19	24
	−3 3 *l*	
1	78	72
5	84	89
7	65	−79
9	39	36
	−4 3 *l*	
3	29	−32
4	85	7
5	25	−39
6	96	37
7	25	−45
	−5 3 *l*	
3	59	60
5	71	−65
7	20	−40
9	48	−57
	−8 3 *l*	
5	26	−44
7	22	−45
	−9 3 *l*	
3	34	−43
7	84	−114
	−11 3 *l*	
3	34	48
5	20	−35
	0 4 *l*	
0	155	162
1	65	−56
2	74	68
3	73	68
5	40	−32
7	63	56
8	54	−33
10	48	9
	1 4 *l*	
0	58	70
2	45	41
4	29	45
6	52	48
	2 4 *l*	
2	47	−20
3	65	−58
4	63	−85
6	56	−66
8	29	−8
	3 4 *l*	
3	48	31
4	67	−76
	4 4 *l*	
0	36	39
3	52	−28
5	47	41
	6 4 *l*	
2	54	34
3	48	27
5	65	−56
	8 4 *l*	
0	66	61
	10 4 *l*	
2	56	5
3	56	−39
4	47	−3
	−1 4 *l*	
2	34	−58
	−2 4 *l*	
3	39	−53
4	22	−6
5	28	29
7	18	−22
	−4 4 *l*	
3	26	−24
5	29	44
	−5 4 *l*	
4	29	−35
	−6 4 *l*	
2	31	−51
4	54	−85
	0 5 *l*	
3	48	42
4	43	10
6	57	−22
7	50	42
	1 5 *l*	
4	37	−43
5	13	−39
	3 5 *l*	
3	65	−71
4	50	56
	−1 5 *l*	
3	34	−22
	−2 5 *l*	
3	29	−30
	−3 5 *l*	
3	31	−57
	−4 5 *l*	
3	22	32
	0 6 *l*	
0	40	−59
6	45	54
	4 6 *l*	
0	39	10
	6 6 *l*	
0	47	−47
	−2 8 *l*	
2	45	15

scattering factor; the values for the anomalous scattering[1] are $\Delta f = -4{\cdot}4$ and $\Delta f'' = 0{\cdot}6$, so that in this case the imaginary part of the correction could be neglected. A Patterson

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[1] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

projection for the $h0l$ zone using $||F_{\mathrm{Cu}}| - |F_{\mathrm{Cr}}||^2$ gave only vanadium-to-vanadium vectors, showing the vanadium to be at $x = 0{\cdot}252$, $z = 0{\cdot}016$, comparison of $|F_{\mathrm{Cu}}|$ with $|F_{\mathrm{Cr}}|$ showed whether the sign of the structure factor was the same or opposite to that of the vanadium contribution. An electron-density map with these signs gave sufficient information for the projection to be solved. Refinement by least-squares gave a final discrepancy factor for the $h0l$ zone of $R = 0{\cdot}18$.

The foreshortening of bonds in the $h0l$ projection gave values for the y-co-ordinates of the sulphur atoms; a three-dimensional Fourier synthesis with the phases from the vanadium atom and the sulphur atoms showed the light atoms of the isothiocyanate groups; and a further Fourier synthesis with the phases from the vanadium atom and the isothiocyanate groups showed the remaining atoms. The structure was then refined by the method of least-squares to a discrepancy factor of $R = 0{\cdot}24$ for non-zero reflections; a comparison of observed and calculated structure factors is given in Table 1. A final three-dimensional difference Fourier

TABLE 2.

Atomic co-ordinates and their standard deviations (in Å) and isotropic thermal parameters and their standard deviations (in Å^2 × 10^3).

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	u^2	$\sigma(\bar{u}^2)$
V(1)	4·23	0·010	1·37	0·013	0·26	0·008	24	2
S(1)	−0·32	0·017	1·84	0·026	1·45	0·016	53	5
S(2)	8·49	0·016	1·70	0·025	−1·68	0·015	45	5
S(3)	5·55	0·017	3·90	0·026	4·18	0·015	47	5
S(4)	2·83	0·016	−0·50	0·025	−4·05	0·015	43	4
O(1)	4·47	0·044	0·01	0·055	1·12	0·038	61	14
O(2)	3·72	0·048	3·26	0·058	−0·83	0·042	68	15
O(3)	5·81	0·057	−0·07	0·067	−4·79	0·050	93	18
O(4)	−6·15	0·048	−0·10	0·061	−3·97	0·042	70	16
O(5)	0·04	0·051	1·57	0·064	−5·18	0·047	82	17
O(6)	0·20	0·053	1·44	0·066	−2·26	0·049	87	17
N(1)	2·30	0·041	1·60	0·058	0·67	0·037	29	11
N(2)	6·04	0·034	1·49	0·052	−0·54	0·031	13	9
N(3)	4·70	0·066	2·65	0·085	1·71	0·060	89	22
N(4)	3·48	0·044	0·41	0·065	−1·53	0·039	33	12
N(5)	2·19	0·037	1·67	0·056	−7·12	0·033	22	10
N(6)	−2·49	0·052	1·97	0·062	−1·53	0·046	50	15
C(1)	1·17	0·049	1·62	0·072	0·99	0·045	26	13
C(2)	7·01	0·051	1·77	0·075	−0·98	0·047	30	14
C(3)	5·03	0·048	3·10	0·071	2·73	0·047	23	13
C(4)	3·28	0·055	−0·08	0·077	−2·61	0·048	35	15

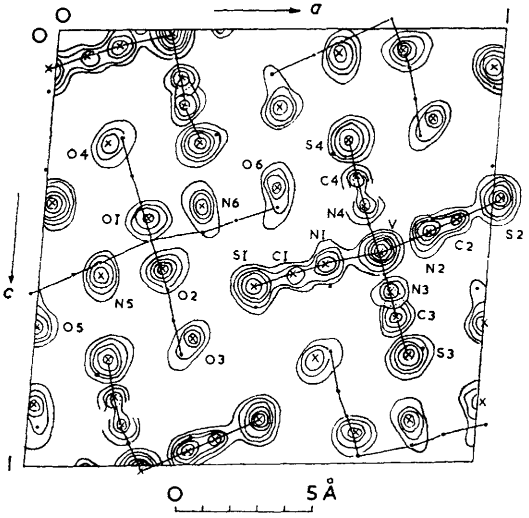

FIG. 1. Composite drawing of the final three-dimensional electron-density map. The contours are at equal arbitrary intervals. The sections shown are those nearest to the atoms marked by crosses. The labelling refers to these atoms. Symmetry-related atoms are shown as dots.

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[2] Dodge, Templeton, and Zalkin, *J. Chem. Phys.*, **1961**, **35**, 55.

synthesis showed the structure to be essentially correct, a composite drawing of the final three-dimensional Fourier map is shown in Fig. 1. The high value of R was attributed to errors in the observed values of the structure amplitudes rather than to any serious errors in the structure.

Results.—The final atomic co-ordinates and isotropic thermal parameters are given in Table 2, the labelling of the atoms corresponds to that in Fig. 1.

Description.—The vanadium atom is co-ordinated to the vanadyl-oxygen atom and to the four nitrogen atoms of the thiocyanate groups. These five atoms are arranged at the vertices of a tetragonal pyramid, as is shown in Fig. 2 in which the weighted mean bond lengths and angles together with their standard deviations are also shown. This arrangement is rather similar to that found in bisacetylacetonevanadyl,[2] in which the angle between the vanadyl-oxygen–vanadium and the vanadium–ligand bond is somewhat larger, 106° as against 97°; a further difference is that in the thiocyanate complex there is a close approach of a water molecule O(2) in the sixth octahedral position.

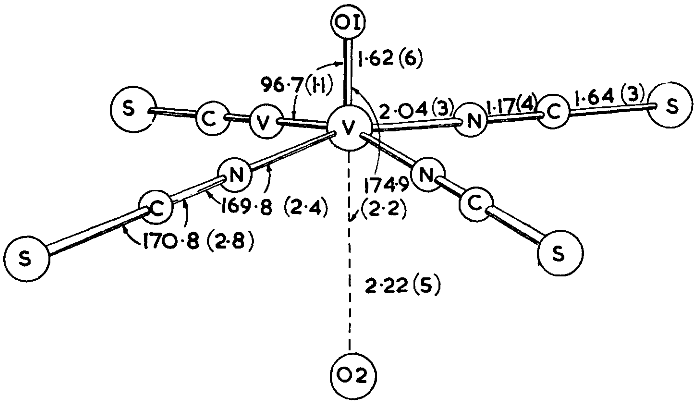

FIG. 2. Bond distances and angles in the complex anion. Estimated standard deviations (× 10^2 for bond lengths) are shown in parentheses.

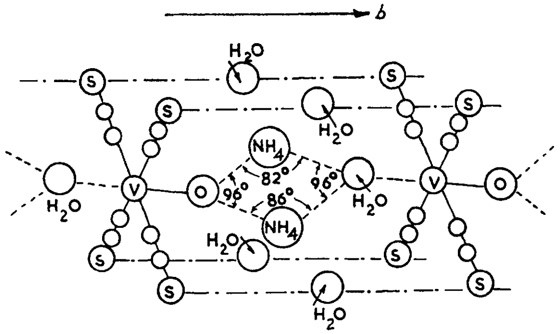

FIG. 3. Arrangement of the complex anions in the crystal.

The structure may be regarded as consisting of chains of anions running parallel to the b-axis, the anions being linked by the two ammonium ions *via* the vanadyl-oxygen and one water molecule O(2). The sulphur atoms are separated from their related atoms in the next unit cell by water molecules (see Fig. 3). Each ammonium ion is surrounded by four oxgyen atoms, arranged at the corners of a distorted tetrahedron.

The vanadyl group and the water molecule O(2) are collinear within experimental error, and make an angle of 32° with the b-axis, the overall effect of the four symmetry-related groups is such as to cause pleochroism corresponding to the vanadyl groups to be parallel to the b-axis.

DISCUSSION

The tetragonal-pyramidal configuration of the $[VO(NCS)_4]^{2-}$ ion may be explained by d^4s-hybridisation; this hybridisation leaves one $3d$-orbital half-filled and available for π-bonding to the vanadyl-oxygen atom. The infrared spectrum shows two V–O stretching frequencies (963 and 982 cm.$^{-1}$) typical of a vanadium-to-oxygen double bond;[3] the bond length is similar to that found in other vanadium-to-oxygen double bonds (see Table 2).

TABLE 2.

Bond distances (Å) in compounds containing vanadium-to-oxygen double bonds.

$VOSO_4,5H_2O$	1·67	Ref. 4	$K_3V_5O_{14}$ *	1·60 and 1·62	Ref. 6
V_2O_5 *	1·585	5	$VOCl_3$	1·56	7
$VO(C_5H_7O_2)_2$	1·56	2			

* Shortest bond(s).

The thiocyanate groups are all bonded to the vanadium through their nitrogen atoms, in agreement with the general rule[8,9] that elements in the first long period form isothiocyanate compounds M–NCS, whereas those in the second long period form thiocyanate or bridged compounds, M–SCN or M–SCN–M. The infrared spectrum showed the S–C stretching frequency $\nu 1(SCN) = 826$ cm.$^{-1}$, as expected for isothiocyanate groups ($690 < \nu 1(SCN) < 720$ cm.$^{-1}$ for thiocyanates, $780 < \nu 1(SCN) < 860$ cm.$^{-1}$ for isothiocyanates[9,10]).

The mean bond lengths and angles in the isothiocyanate group are shown in Fig. 2, the angles V–N–C and N–C–S differ significantly from 180° (by 4·3 and 3·6 standard deviations, respectively). A similar distortion of the thiocyanate group has been observed in Cu $en_2Hg(SCN)_4$.[11] The sulphur–carbon and carbon–nitrogen bond lengths and the V–N–C angle are typical of the values observed in other isothiocyanate compounds (see Table 3).

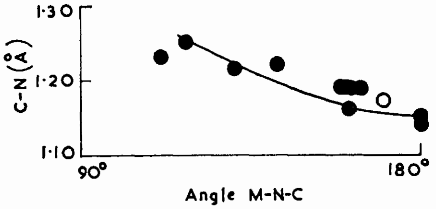

FIG. 4. Plot of carbon–nitrogen bond distances against the angle M–N–C for isothiocyanates. The hollow circle represents the values for $(NH_4)_2VO(NCS)_4,5H_2O$.

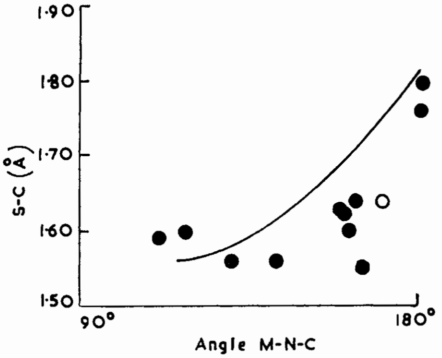

FIG. 5. Plot of sulphur–carbon bond distances against the angle M–N–C for isothiocyanates. The hollow circle represents the values for $(NH_4)_2VO(NCS)_4,5H_2O$.

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[3] Selbin, Holmes, and McGlynn, *Chem. and Ind.*, 1961, 746.
[4] Palma-Vittorelli, Palma, Palumbo, and Sgarlata, *Nuovo Cim.*, 1956, **3**, 717.
[5] Bachmann, Ahmed, and Barnes, *Z. Krist.*, 1961, **115**, 110.
[6] Bystrom and Zvons, *Acta Chem. Scand.*, 1959, **13**, 377.
[7] Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360.
[8] Mitchell and Williams, *J.*, 1960, 1912.
[9] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.
[10] Turco and Pecile, *Nature*, 1961, **191**, 66.
[11] Scouloudi, *Nature*, 1950, **166**, 357; *Acta Cryst.*, 1953, **6**, 651.

TABLE 3.

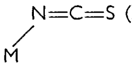
Bond lengths and angles in isothiocyanate and bridged thiocyanate compounds (marked *)

	C–N	S–C	<M–N–C	Ref.
HNCS	1·216	1·561	130·25	12
CH_3NCS	1·22	1·56	142	12
$(NH_4)_2VO(NCS)_4,5H_2O$	1·17	1·64	169·8	—
$NH_4Cr(NH_3)_4(NCS)_4,H_2O$	1·14	1·80	180	13
$pyHCr(NH_3)_2(NCS)_4$	1·15	1·76	180	14
$K_2Co(NCS)_4$	1·23	1·59	111	15
Co $py_2(NCS)_2$	1·19	1·63	158·5	16
$Ni(SC(NH_2)_2)(NCS)_2$	1·16	1·60	161	17
Ni $py_4(NCS)_2$ †	1·07	1·74	165	18
Ni tren $(NCS)_2$	1·19	1·62	159·9	19
Ni en_2 $(NCS)_2$ †	1·20	1·66	—	19, 20
$Ni(NH_3)_4(NCS)_2$ †	1·20	1·61	—	21
AgSCN *	1·19	1·64	162·5	22
$Ag(SCN)Pr^n_3$ *†	1·28	1·76	—	23
$K_2Cd(SCN)_2(NCS)_2,2H_2O$	1·25	1·60	118	24
Cd $etu_2(SCN)_2$ *	1·19	1·55	165	25
α-$(Pt(SCN)Cl(Pr^n_3)_2$ *†	1·31	1·66	147·7	26

† Not shown in Figs. 4 and 5.

A comparison of the values from Table 3 shows that there is some correlation between the M–N–C angle and the carbon–nitrogen and the sulphur–carbon bond distances; in Figs. 4 and 5 these bond lengths are plotted against the angle M–N–C, the curves representing the values calculated by assuming resonance between the forms (I) and (II) and the following bond lengths and angles; C≡N [27] 1·15, C=N [28] 1·26, S=C [27] 1·56, S–C [28]

(I) $M{-}N^+{\equiv}C{-}S^-$



(II)

1·82 Å, and angle M–N–C 180° for case (I) [28] and 116° for case (II),[28], and a shortening of the bonds by 0·03 Å owing to resonance stabilisation for the case when both forms contribute equally.[28] The sulphur–carbon bond lengths are generally shorter than predicted; this may be attributed to *dπ–pπ*-bonding between sulphur and carbon atoms. The values determined for $(NH_4)_2VO(NCS)_4,5H_2O$ are consistent with the observed relation between bond lengths and angles in isothiocyanate groups.

EXPERIMENTAL

The compounds were prepared by the action of the appropriate thiocyanate on an aqueous solution of vanadyl sulphate; the complex was then extracted with ethyl acetate from which it was recrystallised (cf. Koppel and Goldman [29]).

Intensity Measurements.—Three-dimensional intensities were obtained from equi-inclination

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[12] Beard and Dailey, *J. Amer. Chem. Soc.*, 1949, **71**, 929.
[13] Saito, Takeuchi, and Pepinsky, *Z. Krist.*, 1955, **106**, 476.
[14] Takeuchi and Pepinsky, *Z. Krist.*, 1957, **109**, 29.
[15] Zhdanov, Tishchenko, and Zvonkova, *Zhur. fiz. Khim.*, 1950, **24**, 1338.
[16] Porai-Koshits and Tishchenko, *Kristallografiya*, 1958, **3**, 686.
[17] Nardelli, Brabianti, and Fava, *Gazzetta*, 1957, **87**, 1209.
[18] Porai-Koshits, *Kristallografiya*, 1958, **3**, 686.
[19] Rasmussen, *Acta Chem. Scand.*, 1959, **13**, 2009.
[20] Lingafelter, *Nature*, 1958, **182**, 1730.
[21] Yukhno and Porai-Koshits, *Kristallografiya*, 1957, **2**, 239.
[22] Lindquist, *Acta Cryst.*, 1957, **10**, 29.
[23] Turco, Panattoni, and Frasson, *Nature*, 1960, **187**, 772.
[24] Zvonkova, *Zhur. fiz. Khim.*, 1952, **26**, 1798.
[25] Cavalca, Nardelli, and Fava, *Acta Cryst.*, 1960, **13**, 125.
[26] Owston and Rowe, *Acta Cryst.*, 1960, **13**, 253.
[27] Sutton *et al.*, " Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, 1958.
[28] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 3rd edn.
[29] Koppel and Goldmann, *Z. anorg. Chem.*, 1903, **36**, 281.

Weissenberg photographs about three principal axes (up to *hk*8, *h*3*l*, and 8*kl*) by the multiple film technique; the intensities were measured visually with a calibration strip. No corrections were made for absorption, as approximately cylindrical crystals of diameter 0·1 mm. were used with Cu-K_a radiation.

For the *h*0*l* intensities with Cu-K_a and Cr-K_a, the same crystal was used for both sets of measurements; the crystal was approximately cylindrical with mean radius 0·11 mm., *i.e.*, $\mu r = 1{\cdot}0$ for Cu-K_a and $\mu r = 1{\cdot}8$ for Cr-K_a. The values of the absorption corrections applied were those from the International Tables.[30]

Refinement.—The function minimised by least-squares was $R' = \sum w(|F_o| - |F_c|)^2$, where the weighting factor, *w*, was $1/(4 + |F_o|)$. The atomic scattering factors used were those of Thomas and Fermi [30] for vanadium, Tomiie and Stam [31] for sulphur, and Berghuis *et al.*[32] for carbon, nitrogen, and oxygen.

Calculations were carried out on the Leeds University and the Durham University Ferranti Pegasus computers with programmes written by Cruickshank, Pilling, *et al.*,[33] and Samet. The infrared spectra were recorded on a Grubb-Parsons spectrometer, the samples being prepared in the form of potassium bromide discs.

Some of the equipment used was provided by the Royal Society and Imperial Chemical Industries Limited. The author is indebted to Dr. Mary R. Truter for her helpful advice, to the D.S.I.R. for a maintenance award whilst at Leeds University, and to British Titan Products for a Research Fellowship at King's College.

DEPARTMENT OF STRUCTURAL AND INORGANIC CHEMISTRY, THE UNIVERSITY, LEEDS 2.
DEPARTMENT OF CHEMISTRY, KING'S COLLEGE, NEWCASTLE UPON TYNE 1.

[Present address: KEMISK INSTITUT,
AARHUS UNIVERSITET, DENMARK.]

[*Received, February 27th*, 1963.]

[30] " International Tables for the Determination of Crystal Structures," Borntrager, Berlin, 1935.
[31] Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.
[32] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[33] Cruickshank, Pilling, and (in part) Bujosa, Lovell, and Truter, " Computing Methods and the Phase Problem in *X*-ray Crystal Analysis," Pergamon Press, London, 1961, p. 32.