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The Structure of a Chelated Dinuclear Peroxytitanium(IV)

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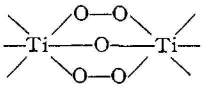
The red-orange dinuclear product formed by mixing Ti(IV) and H_2O_2 can be complexed with various chelating agents. The potassium salt of the chelate with dipicolinic acid forms yellow crystals with the composition $K_2[Ti_2O_5(C_7H_3O_4N)_2]\cdot 5H_2O$. The space group is $C2/c$; the lattice constants are $a = 8.988 \pm 0.002$, $b = 27.505 \pm 0.005$, $c = 9.533 \pm 0.003$ Å, and $\beta = 92.14 \pm 0.02°$. There is a half formula unit per asymmetric unit. The structure was solved from film data by a combination of Patterson and direct methods and was refined to $R = 11.3\%$ for 1439 observed reflections. The dinuclear complex has the symmetry C_2. The titanium atoms are coordinated approximately pentagonal bipyramidally sharing an apical μ-oxygen. In each bipyramid, the peroxy group and the dipicolinic acid ligand occupy the equatorial sites, and the remaining apex is occupied by water. In the TiO_2 ring, the O–O distance is 1.45 ± 0.01 Å, the Ti–O distances are 1.872 ± 0.007 and 1.905 ± 0.007 Å, and the O–Ti–O angle is $45.2 \pm 0.4°$. The complexes are linked into layers by hydrogen bonds; all peroxy groups in one layer point to one side. The potassium ions are in holes between two layers, the peroxy sides of which point toward each other.

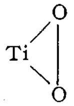
Introduction

Mühlebach, Müller, and Schwarzenbach[2] showed that the strongly colored 1:1 adducts formed from Ti(IV) and H_2O_2 are binuclear. They contain the group $Ti_2(O_2)_2O\cdot aq^{2+}$ and it was suggested that the metal atoms are bridged by a μ-oxygen and two μ-peroxy groups. This leads to the postulated structure



the sixfold coordination being completed by H_2O or the ligand atoms of a chelating agent. Assuming regular octahedra, a Ti–O distance of 1.94 Å, and an O–O distance between 1.32 and 1.48 Å, this would be a remarkably strain-free complex with a Ti–O–Ti angle between 103 and 107°. It requires the grouping Ti–O–O–Ti to be planar. Bidentate peroxy groups, however, do not seem to lead to planar configurations. Schaefer and Marsh[3] reported a torsion angle of 146° around the O–O bond in $(NH_3)_5Co(O_2)Co(NH_3)_5{}^{4+}$, and H_2O_2 is known to be nonplanar with one exception,[4] the torsion angle depending rather sensitively on the surrounding of the molecule.[5,6] On the other hand, the configuration in the superoxo ion $(NH_3)_5Co(O_2)Co(NH_3)_5{}^{5+}$ has been shown to be planar with an O–O distance of about 1.32 Å.[7,8] Thus the bridges in the postulated $Ti_2O_5\cdot aq^{2+}$ ion might be expected to be superoxy rather than peroxy groups.

Another possible configuration for the complex contains



rings analogous to the majority of the peroxides of transition metals whose structures are known.[9] The only titanium–peroxy compound crystallized so far is $(NH_4)_3[Ti(O_2)F_5]$. It was reported by Peyronel[10] to be isomorphous with $(NH_4)_3[ZrF_7]$,[11] indicating the TiO_2 ring configuration and a seven-coordinated titanium. The structure was described as disordered and a distinction between oxygen and fluorine was not possible; thus very little information about the stereochemistry of the titanium–peroxy grouping was provided. Mühlebach, Müller, and Schwarzenbach[2] obtained a stable complex of $Ti_2(O_2)_2O\cdot aq^{2+}$ with dipicolinic acid (2,6-pyridinedicarbonic acid) which they crystallized in the form of the potassium salt, having the chemical composition $K_2[Ti_2O_5(H_3NC_7O_4)_2]\cdot 5H_2O$. After completion of this structure determination, they showed that one of the water molecules is easily lost below 30% relative humidity. The stability of this complex indicates that the peroxy groups may not bridge the titanium atoms, since the dipicolinic acid molecules would then have to be attached facially on the octahedra instead of equatorially, necessitating considerable distortions.

Experimental Section

Bright yellow prismatic crystals of the complex were supplied by Dr. G. Schwarzenbach. During the X-ray work, they disintegrated slowly into a fine yellow powder, possibly through the loss of water of crystallization. This was realized only after a considerable part of the intensity data had already been collected. The space group, $C2/c$, was determined on the basis of the extinctions observed on precession photographs, from a strong indication of centricity by the Howells–Phillips–Rogers[12] test and by the distribution of the E values.[13a] To determine the lattice constants, 4ϑ angles of 16 independent reflections were

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[2] J. J. Mühlebach, K. Müller, and G. Schwarzenbach, *Inorg. Chem.*, **9**, 2381 (1970).

[3] W. P. Schaefer and R. E. Marsh, Abstracts, American Crystallographic Association Summer Meeting, Minneapolis, Minn., Aug 1967.

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[7] W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 740 ((1965).

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[11] G. C. Hampson and L. Pauling, *J. Amer. Chem. Soc.*, **60**, 2702 (1938).

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TABLE I

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a]

	10^4x	10^4y	10^4z	$10^4\beta_{11}$	$10^5\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ti	3398 (2)	4166.4 (5)	3621 (2)	72 (3)	88 (2)	141 (2)	1 (1)	−53 (3)	−2 (1)
K(1)[b]	5000	5376 (1)	2500	150 (6)	109 (4)	192 (5)	0	−87 (8)	0
K(2)[c]	0976 (7)	4806 (3)	0587 (9)	194 (11)	302 (13)	425 (17)	−83 (6)	−412 (22)	154 (8)
O(1)	0633 (8)	3376 (2)	0862 (8)	114 (10)	151 (10)	181 (11)	2 (5)	−117 (17)	−9 (5)
O(2)	6138 (8)	3298 (3)	6096 (8)	121 (11)	170 (11)	180 (11)	13 (5)	−124 (17)	−3 (5)
O(3)	1874 (6)	3962 (2)	2046 (7)	78 (9)	118 (8)	147 (9)	10 (4)	−45 (14)	9 (4)
O(4)	4687 (7)	3906 (2)	5308 (7)	83 (10)	108 (8)	137 (8)	3 (4)	−67 (13)	−4 (4)
O(5)	3579 (8)	4774 (2)	4492 (9)	129 (12)	85 (7)	268 (14)	1 (4)	−122 (19)	−14 (5)
O(6)	2587 (9)	4796 (2)	3256 (10)	123 (13)	124 (9)	279 (16)	12 (5)	−120 (21)	6 (6)
O(7)[b]	5000	4177 (3)	2500	107 (15)	169 (14)	116 (11)	0	−112 (20)	0
O(8)	1546 (8)	4024 (3)	4981 (8)	85 (10)	177 (11)	148 (9)	−11 (5)	−1 (14)	2 (5)
O(9)[d]	1974 (11)	3976 (4)	7801 (9)	260 (18)	257 (17)	173 (13)	32 (9)	−145 (24)	14 (7)
N	3358 (7)	3377 (2)	3536 (8)	59 (10)	105 (9)	140 (10)	−13 (4)	−51 (15)	−11 (5)
C(1)	1583 (10)	3524 (3)	1714 (10)	76 (13)	118 (11)	140 (12)	−3 (5)	−28 (19)	−8 (6)
C(2)	2453 (9)	3156 (3)	2550 (9)	54 (11)	113 (11)	143 (12)	−17 (5)	−20 (18)	−13 (5)
C(3)	2410 (11)	2655 (3)	2430 (11)	125 (16)	106 (12)	166 (15)	−9 (6)	−40 (24)	−12 (6)
C(4)	3402 (10)	2377 (3)	3336 (11)	104 (15)	113 (11)	191 (15)	−3 (6)	−15 (23)	−11 (7)
C(5)	4343 (10)	2620 (3)	4362 (10)	81 (12)	122 (11)	147 (12)	−10 (6)	10 (18)	5 (6)
C(6)	4268 (8)	3130 (3)	4385 (8)	68 (11)	72 (8)	114 (9)	−1 (4)	−7 (15)	8 (4)
C(7)	5113 (10)	3464 (3)	5374 (9)	102 (14)	126 (12)	102 (10)	16 (6)	−50 (17)	−6 (5)

[a] The temperature factor expression used is $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\}$. The least-squares standard errors are indicated in parentheses. [b] Site symmetry 2. [c] Occupancy $^1/_2$. [d] Crystal water.

measured at room temperature on a Picker diffractometer using CuKα radiation (λ 1.5418 Å). Each reflection was carefully centered in the counter window at $+2\vartheta$ and -2ϑ with the χ, ω, and 2ϑ circles. The refinement by least squares was made on sin ϑ. The density was measured by the flotation method in a mixture of carbon tetrachloride and methyl iodide. The crystal data are as follows: chemical composition $C_{14}H_{16}N_2O_{18}K_2Ti_2$; formula weight 674.28; monoclinic, space group $C2/c$, systematic absences hkl absent for $h + k = 2n + 1$, $h0l$ absent for $h, l = 2n + 1$; $Z = 4$; $a = 8.988$ (2), $b = 27.505$ (5), $c = 9.533$ (3) Å; $\beta = 92.14$ (2)^0; $D_m = 1.893$ (5), $D_x = 1.901$ g cm^{-3}; $\mu_{\text{Cu K}\alpha} = 99.59$, $\mu_{\text{Mo K}\alpha} = 11.44$ cm^{-1}. Integrated intensity data ($0kl$–$7kl$) were collected on equiinclination Weissenberg photographs using a Nonius integrating camera and Cu Kα radiation. Since they were disintegrating, two different crystals had to be used. Their dimensions were 0.35 and 0.38 mm along a, 0.14 and 0.10 mm along b, and 0.24 and 0.20 mm along c, respectively. Their morphology was dominated by the forms $\{021\}$ and $\{010\}$, while $\{110\}$ and $\{10\bar{1}\}$ terminated the prism. A third crystal with similar shape and overall dimensions was used for recording intensity data ($hk0$–$hk5$) on a Supper precession camera using Mo Kα radiation.

The intensities were measured with a densitometer (Baird-Atomic, Inc., Model CB). In addition to the usual geometrical corrections, the Weissenberg data were corrected for absorption, using a modified version of the program of C. Burnham.[13b] The transmission factors ranged from 4.8 to 2.2. The ratios of largest and smallest transmission factors of reflections in one layer did not exceed 1.98. The corrected intensities were then placed on the same relative scale by the least-squares method of Hamilton, Rollett, and Sparks[14] using 918 reflections common to the a-axis and c-axis photographs. A weighting system analogous to the one described by Hughes[15] was used. The a-axis data were weighted three times more heavily than the c-axis data, because of the higher accuracy of the integrated Weissenberg data. The standard deviations of the mean $\overline{F^2} = \Sigma w_i F_i^2/\Sigma w_i$ were computed as $[K/\Sigma w_i]^{1/2}$, w_i being the weights of the individual scaled F_i^2; K is the "error of fit," $(1/m)\Sigma w_k(\Delta F_k^2)^2$, where m is the number of degrees of freedom in the least-squares procedure, and ΔF_k^2 are the deviations of the individual F_k^2 from their respective mean values, the sum extending over *all* measurements. These standard deviations turned out to be about 15% of the F^2 values. Because of the decay of the crystals, the effective exposure time varied considerably for different layers, resulting in many unobserved reflections, especially for large diffraction angles. The number of unique reflections measured was 2507, only 1439 of which were observed.

The calculations were made on an IBM 360/75 computer; most programs used were written or modified in this laboratory. The distances and angles together with their standard deviations were computed using the Oak Ridge crystallographic function and error program, "ORFFE-II," by Busing, Martin, and Levy (ORNL-TM-306); the illustrations were drawn with the Oak Ridge thermal ellipsoid plot program for crystal-structure illustrations, "ORTEP," by Johnson (ORNL-3794).

Structure Determination

Since there are four formula units per unit cell, the complex must occupy a twofold axis or a center of symmetry. Assuming bridging peroxy groups, the distance between the two titanium atoms should be about 3.0–3.1 Å and a corresponding peak should appear on the Harker section. In the case of the TiO_2 ring configuration, the distance between the titanium atoms is certainly longer, however less predictable, but it can be expected to be less than 4 Å.

A three-dimensional Patterson map sharpened with a negative overall temperature factor did not reveal the structure immediately. The most prominent feature on the Harker section was a peak of about half the height of the origin peak, corresponding to a distance of about 3.6 Å. Attempts to find the peaks corresponding to two heavy atoms per asymmetric unit (Ti and K) failed. Application of direct methods using a computer program,[16] based on a reiterative application of Sayre's equation,[17a] led to two solutions, one of which was compatible with the Patterson map. It revealed one peak in a general position (Ti) and one on the twofold axis (K). The rest of the structure was obtained through two successive Fourier maps. One of the potassium ions per formula unit turned out to be

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(17) (a) D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952); (b) No. 384 in ref 13b.

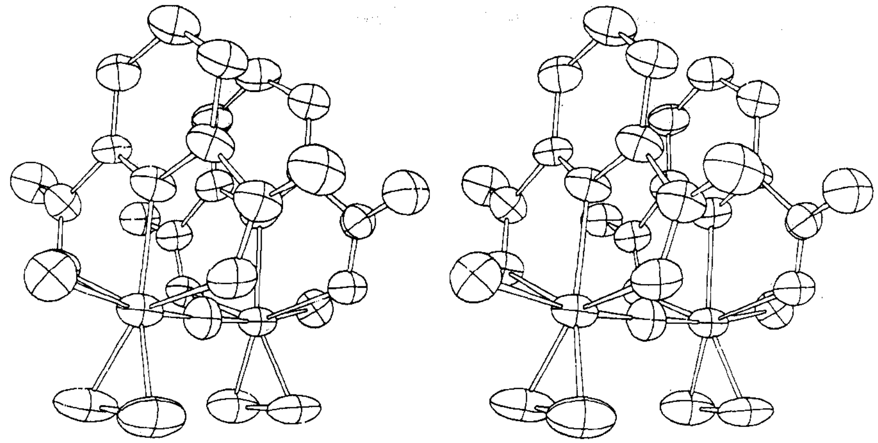

Figure 1.—View of the complex, drawn with 50% probability ellipsoids.

disordered with half-atoms occupying a general eightfold position. The intensity data exclude an ordered structure with the acentric space group symmetry *Cc*, since the difference between 12 (*C*2/*c*) and 16 (*Cc*) heavy atoms per cell must be detectable in the centricity tests or in the Patterson function. One of the five water molecules per formula unit, *i.e.*, a half water per asymmetric unit, could not be located, either at this stage or later.

The structure was refined by full-matrix least squares, using a modified version of the program by Gantzel, Sparks, and Trueblood.[17b] The weights used were derived from the standard deviations of the $|F|^2$ discussed above. Refinement with isotropic temperature factors reduced the *R* value to 21.3%; with anisotropic temperature factors, the *R* value for the observed reflections dropped to 11.3%.

A difference Fourier synthesis based on the final parameters showed three peaks between 1.0 and 1.4 $e^-/Å^3$ as well as holes near the sites of the potassium and titanium atoms. The disordered potassium ion K(2) (Table I) has a very high temperature factor that probably does not describe its electron density distribution appropriately. The highest residual densities were found on the fringes of this ion. The highest peak away from known atoms (1.3 $e^-/Å^3$) was found on the twofold axis. All the other peaks were lower than 0.9 $e^-/Å^3$. The low accuracy of the intensity data did not permit identification of any of these peaks with the missing water molecule, and no hydrogen atoms could be found. Since the crystals easily lose one of the five water molecules per formula unit below 30% relative humidity, it is not too surprising that one water could not be located. It was probably lost to the dry desert air at least partially during the collection of the intensities.

The atomic positional and thermal parameters are given in Table I, and the observed and calculated structure factors, in Table II.

Description of the Complex and the Crystal Structure

The configuration of the complex is illustrated in Figure 1; the distances and angles are given in Figures 2 and 3 and in Table III. The least-squares planes

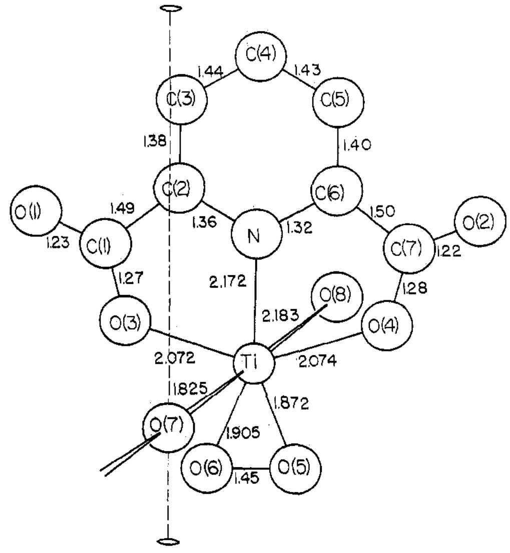

Figure 2.—Distances in the complex. The esd's are given in Table III. For the distances in the dipicolinic acid they are 0.012 Å.

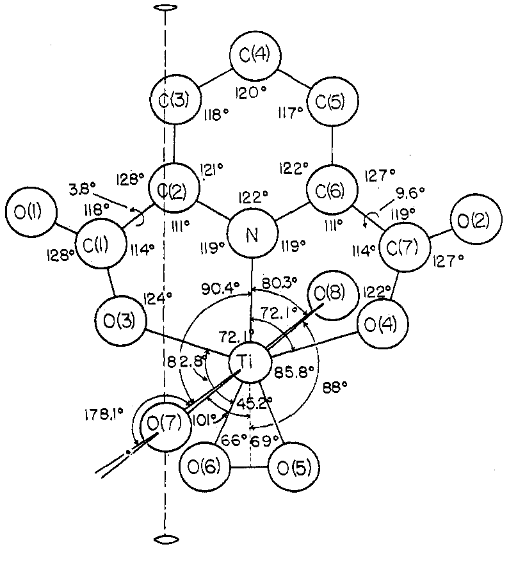

Figure 3.—Angles in the complex. The esd's are given in Table III. For the angles in the dipicolinic acid they are 0.8°.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS (SCALE FACTOR 3.048)

H= 0, L= 0		
2	109	103
4	134	-136
6	48	-28
8	44	34
10	73	79
12	244	240
14	175	-156
16	174	-177
18	80	-72
20	31	-33
22	7*	-7
24	17	-4
26	35	36
28	26	-24
30	27	-23
32	24	-20
34	4*	6
H= 1, L= 0		
1	110	113
3	63	-37
5	22	-8
7	104	-86
9	84	-68
11	34	28
13	12	-11
15	43	-39
17	31	-34
19	62	-61
21	15	-8
23	28	25
25	48	44
27	28	24
29	15	-14
31	16	-15
33	5*	2
H= 2, L= 0		
0	58	-65
2	3*	-8
4	16	6
6	124	102
8	21	-27
10	101	-98
12	70	-67
14	17	-15
16	7*	12
18	40	37
20	20	19
22	16	-14
24	20	22
26	29	26
28	26	25
30	15	12
32	6*	11
34	14	-6
H= 3, L= 0		
1	68	52
3	44	-43
5	85	-71
7	17	22
9	116	112
11	98	-102
13	130	-125
15	68	-68
17	41	40
19	75	68
21	65	66
23	54	-61
25	23	-28
27	33	37
29	43	49
31	16	16
33	4*	7
35	43	-23
37	31	-21
H= 4, L= 0		
0	58	-55
2	12	-10
4	40	43
6	14	14
8	25	23
10	25	-24
12	97	-91
14	42	-36
16	21	27
18	27	30
20	16	27
22	8*	1
24	25	-22
26	27	19
28	36	24
30	19	14
32	7*	9
34	6*	-7
36	24	-18
H= 5, L= 0		
1	77	68
3	50	70
5	3*	6
7	18	17
9	31	-34
11	15	-17
13	24	24
15	13	3
17	56	-57
19	6*	-9
21	20	-23
23	19	14
25	30	32
27	5*	6
29	16	-15
31	3*	-3
H= 6, L= 0		
0	132	115
2	47	75
4	87	-114
6	108	-121
8	14	-12
10	11	12
12	42	43
14	15	18
16	84	-83
18	37	-33
20	15	16
22	7*	5
24	45	45
26	23	24
28	5*	1
30	8	-10
H= 7, L= 0		
1	86	85
3	6*	10
5	25	-26
7	6*	-7
9	23	-27
11	44	38
13	37	32
15	27	-26
17	48	-39
19	7*	-3
21	35	-31
23	36	27
25	33	25
27	6*	-1
29	21	-11
H= 8, L= 0		
0	6*	6
2	25	24
4	34	33
6	22	29
8	7*	-12
10	24	-18
12	27	-22
14	10	-9
16	7*	-10
18	20	-16
20	7*	-20
22	7*	-1
24	6*	-2
26	6*	-2
H= 9, L= 0		
1	7*	-10
3	7*	-5
5	22	19
7	42	38
9	7*	-4
11	34	-30
13	29	-21
15	14	-8
17	10	12
19	40	33
21	6*	5
23	22	-14
25	22	-12
H= 10, L= 0		
0	53	-49
2	7*	7
4	14	11
6	20	20
8	7*	6
10	6*	-9
12	41	-34
14	6*	-7
16	6*	3
18	23	20
H= 11, L= 0		
1	6*	0
3	6*	-10
5	6*	4
7	6*	-6
9	20	-19
11	5*	-3
13	6*	7
H= 12, L= 0		
0	51	47
2	5*	1
4	5*	-8
6	17	-7
8	14	-13
10	4*	3
12	15	24
H= 0, L= 1		
2	205	222
4	11	9
6	14	13
8	57	-54
10	105	-94
12	18	23
14	156	145
16	112	109
18	52	48
20	15	-17
22	8*	5
24	8*	4
26	27	23
28	29	26
30	20	-18
32	31	-29
34	24	-24
H= 1, L= 1		
1	89	91
3	75	82
5	162	177
7	210	-190
9	193	-175
11	36	-35
13	83	85
15	103	100
17	111	105
19	25	-21
21	51	-48
23	7*	-5
25	21	20
27	42	42
29	7*	-7
31	32	-33
33	34	-34
H= -1, L= 1		
1	61	-69
3	79	-94
5	30	-47
7	47	-58
9	51	-55
11	60	-57
13	57	-52
15	12	-7
17	30	28
19	22	21
21	7*	9
23	7*	8
25	8*	8
27	8*	0
29	7*	-3
31	6*	-3
33	5*	-4
H= 2, L= 1		
2	35	26
4	42	25
6	12	-22
8	12	-21
10	27	-26
12	11	2
14	56	48
16	84	71
18	35	34
20	23	21
22	8*	-1
24	9*	-9
26	26	18
28	17	8
30	14	-15
32	15	-17
34	14	-16
H= -2, L= 1		
2	221	-240
4	104	-98
6	170	-139
8	138	-105
10	61	-56
12	80	-84
14	170	-116
16	54	-60
18	8*	-13
20	52	46
22	34	28
24	30	32
26	9*	-5
28	34	-33
30	8*	5
32	16	20
34	12	16
H= 3, L= 1		
1	44	-49
3	77	-96
5	40	-50
7	138	-126
9	52	-47
11	47	42
13	71	-63
15	88	-87
17	8*	6
19	8*	4
21	40	38
23	56	57
25	31	-32
27	32	-34
29	7*	1
31	6*	1
33	4*	6
H= -3, L= 1		
1	65	-84
3	65	-61
5	122	-141
7	96	85
9	66	60
11	7*	-3
13	35	-38
15	7*	-2
17	15	-11
19	50	51
21	54	58
23	28	28
25	9*	2
27	35	-38
29	7*	-10
31	6*	5
33	5*	9
H= 4, L= 1		
2	48	-51
4	137	-145
6	29	22
8	20	-11
10	61	52
12	28	25
14	35	-29
16	81	-83
18	79	76
20	38	32
22	72	71
24	12*	3
26	12*	-19
28	27	-30
30	11*	-0
32	8*	9
H= -4, L= 1		
2	34	-44
4	26	-32
6	19	11
8	16	-14
10	40	-35
12	21	-20
14	22	10
16	22	25
18	37	35
20	12*	1
22	12*	-7
24	12*	14
26	12*	2
28	11*	-8
30	11*	-7
32	8*	-12
H= 5, L= 1		
1	13	-16
3	49	-59
5	29	-38
7	5*	-5
9	5*	1
11	6*	5
13	22	-17
15	36	-35
17	19	24
19	31	33
21	22	22
23	15	10
25	6*	-4
27	12	-8
29	9	2
31	3*	-1
H= -5, L= 1		
1	27	40
3	57	82
5	3*	4
7	20	-20
9	73	-79
11	68	-75
13	72	60
15	117	111
17	33	28
19	6*	7
21	23	-20
23	23	-23
25	52	46
27	32	37
29	13	-11
31	17	-16
H= 6, L= 1		
2	66	86
4	15	15
6	101	-99
8	91	-92
10	102	-100
12	7*	-10
14	34	29
16	8*	3
18	28	-29
20	16	16
22	21	-16
24	7*	8
26	17	19
28	5*	11
H= -6, L= 1		
2	14	16
4	56	72
6	32	-37
8	30	-31
10	64	-64
12	24	-26
14	38	36
16	84	89
18	25	-26
20	7*	-6
22	40	-41
24	7	8
26	17	14
28	16	15
30	3*	-10
H= 7, L= 1		
1	47	60
3	63	64
5	24	27
7	55	-54
9	74	-71
11	26	-30
13	58	63
15	46	42
17	10*	14
19	10*	13
21	31	-25
23	10*	-19
25	29	23
27	27	22
H= -7, L= 1		
1	10*	-13
3	10*	-13
5	10*	-7
7	10*	-10
9	19	-22
11	22	-26
13	10*	-7
15	19	21
17	16	13
19	10*	8
21	10*	-2
23	10*	3
25	11*	8
27	11*	6
H= 8, L= 1		
2	10*	11
4	10*	15
6	10*	-2
8	24	-24
10	10*	-20
12	10*	1
14	10*	8
16	26	23
18	22	22
20	11*	-7
22	11*	-18
24	11*	-2
H= -8, L= 1		
2	48	-51
4	31	-27
6	10*	19
8	10*	5
10	27	30
12	10*	5
14	16	-19
16	10*	2
18	27	28
20	11*	0
22	31	30
24	11*	10
H= 9, L= 1		
1	10*	-21
3	10*	18
5	10*	-12
7	10*	-17
9	10*	11
11	35	38
13	11*	3
15	11*	4
17	11*	-3
19	19	17
21	34	33
H= -9, L= 1		
1	25	-33
3	41	-44
5	32	-34
7	10*	12
9	20	20
11	10*	2
13	34	-41
15	22	-21
17	11*	-1
19	11*	1
21	24	21
H= 10, L= 1		
2	50	-55
4	11*	10
6	11*	-17
8	11*	-11
10	34	43
12	11*	8
14	43	-33
H=-10, L= 1		
2	11*	-11
4	11*	-13
6	11*	-8
8	11*	-7
10	11*	-6
12	11*	-10
14	11*	-1
16	11*	-2
18	10*	1
20	10*	6
H=-11, L= 1		
1	21	25
3	11*	6
5	11*	7
7	11*	-4
9	22	-21
11	20	-20
H=-12, L= 1		
2	28	30
4	10*	-6
6	10*	6
8	10*	-1
10	22	-25
H= 0, L= 2		
0	36	-54
2	13	-10
4	14	-19
6	103	102
8	38	34
10	12	14
12	5*	7
14	10	6
16	11	7
18	30	22
20	7*	-1
22	40	-42
24	25	-24
26	22	-23
28	18	-13
30	9	-8
32	6*	6
34	10*	-3
H= 1, L= 2		
1	176	-188
3	118	-134
5	23	12
7	99	100
9	125	109
11	88	-105
13	57	-55
15	35	29
17	112	112
19	91	79
21	42	40
23	92	-87
25	49	-47
27	24	16
29	29	28
31	6*	4
33	5*	5
35	25	-14
H= -1, L= 2		
1	95	115
3	122	-117
5	41	-34
7	36	-28
9	20	24
11	124	118
13	55	51
15	13	-11
17	7*	-3
19	44	-42
21	24	-19
23	10	-11
25	7*	4
27	17	-11
29	36	-36
31	26	-25
33	5*	0
35	18	11
H= 2, L= 2		
0	197	-175
2	138	-116
4	46	-24
6	29	-12
8	103	107
10	51	51
12	117	-105
14	44	-40
16	80	74
18	90	79
20	50	51
22	27	-22
24	85	-79
26	16	-12
28	15	17
30	7*	12
32	11	9
34	10*	-6
H= -2, L= 2		
0	511	549
2	132	-109
4	104	-105
6	32	29
8	41	26
10	49	42
12	240	216
14	24	-21
16	37	-43
18	20	-19
20	20	-24
22	19	-14
24	8*	-18
26	8*	14
28	37	-38
30	31	-33
32	20	-21
34	10*	7
H= 3, L= 2		
1	4*	-10
3	20	9
5	16	-18
7	76	66
9	30	34
11	26	29
13	33	36
15	31	31
17	8*	-7
19	37	38
21	19	-21
23	13	-18
25	8*	-6
27	8*	-12
29	18	-20
31	6*	-1
33	4*	-3
H= -3, L= 2		
1	55	-68
3	93	-106
5	46	-50
7	59	-56
9	20	-11
11	44	47
13	27	23
15	14	18
17	24	21
19	8*	-5
21	17	14
23	8*	8
25	8*	5
27	8*	-0
29	7*	-11
31	6*	-4
33	4*	5
H= 4, L= 2		
0	76	-62
2	35	-28
4	160	-157
6	124	-118
8	25	12
10	18	11
12	65	55
14	97	86
16	17	-16
18	11*	2
20	23	21
22	11*	-11
24	33	33
26	23	19
28	11*	-8
30	30	-25
32	8*	-17
H= -4, L= 2		
0	150	-183
2	89	-116
4	24	-23
6	85	82
8	33	29
10	35	-41
12	19	-26
14	36	29
16	58	63
18	68	73
20	32	38
22	27	-22
24	20	-13
26	11*	-5
28	11*	9
30	10*	8
32	8*	8
H= 5, L= 2		
1	102	98
3	52	-61
5	99	-100
7	5*	-5
9	5*	11
11	105	100
13	68	67
15	27	-29
17	31	-26
19	22	24
21	40	-37
23	21	18
25	17	17
27	15	-14
29	26	-21
31	9	-10
H= -5, L= 2		
1	54	-68
3	16	-19
5	27	28
7	57	60
9	61	66
11	62	-62
13	49	-46
15	6*	1
17	48	44
19	42	34
21	26	26
23	74	-66
25	47	-47
27	9	3
29	21	19
31	10*	5
H= 6, L= 2		
0	4*	-7
2	5*	-2
4	9	-11
6	6*	4
8	7*	2
10	27	26
12	13	9
14	8*	-0
16	8*	1
18	8*	0
20	13	-18
22	7*	-6
24	20	-14
26	10	-17
28	4*	-8
30	10*	-7
H= -6, L= 2		
0	38	-50
2	26	-28
4	7	8
6	14	15
8	17	19
10	7*	11
12	13	-11
14	8*	1
16	14	17
18	21	19
20	13	16
22	8*	-3
24	25	-23
26	10	-10
28	5*	-3
30	10*	4
H= 7, L= 2		
1	41	-45
3	20	-14
5	63	61
7	95	86
9	9*	-0
11	35	-36
13	19	-15
15	9*	11
17	38	33
19	39	35
21	30	-20
23	60	-41
25	41	-29
27	10*	-7
29	16	9
H= -7, L= 2		
1	9*	-9
3	9*	12
5	9*	-6
7	17	12
9	9*	-14
11	9*	6
13	54	47
15	24	26
17	25	-27
19	10*	-4
21	20	-21
23	10*	3
25	10*	12
27	10*	-11
29	26	-22
H= 8, L= 2		
0	87	-73
2	9*	4
4	9*	5
6	36	39
8	40	37
10	10*	14
12	52	-46
14	10*	-17
16	24	12
18	52	44
20	21	17
22	25	-25
24	36	-30
26	29	-26
28	18	10
H= -8, L= 2		
0	31	30
2	19	23
4	59	-52
6	43	-43
8	9*	-0
10	10*	4
12	46	42
14	34	33
16	40	-41
18	17	-18
20	10*	2
22	10*	-7
24	24	22
26	10*	2
28	10*	-10
H= 9, L= 2		
1	36	-39
3	34	-37
5	10*	-8
7	10*	-3
9	10*	-7
11	10*	-1
13	10*	5
15	10*	7
17	18	19
19	16	16
H= -9, L= 2		
1	15	15
3	10*	-4
5	10*	-17
7	10*	-1
9	10*	-6
11	30	30
13	27	24
15	10*	-2
17	10*	-13
19	10*	7
H= 10, L= 2		
0	40	39
2	10*	-17
4	10*	-8
6	10*	1
8	10*	-10
10	10*	-0
12	41	34
H=-10, L= 2		
0	38	-37
2	14	-12
4	14	18
6	27	31
8	10*	-1
10	10*	-14
12	10*	-13
H= 11, L= 2		
1	20	20
3	10*	-4
5	28	-28
7	26	-27
9	10*	5
11	33	30
H=-11, L= 2		
1	26	-25
3	10*	-7
5	10*	11
7	26	22
9	10*	-1
11	18	-18
H=-12, L= 2		
0	33	-28
H= 0, L= 3		
2	53	51
4	104	102
6	92	88
8	71	61
10	37	26
12	36	36
14	65	59
16	59	48
18	7*	-8
20	34	-29
22	31	-30
24	8*	-9
26	30	26
28	7*	10
30	6*	-7
32	5*	-3
34	12*	-1
H= 1, L= 3		
1	18	-18
3	9	-13
5	44	43
7	59	-41
9	15	17
11	89	90
13	34	-31
15	88	-89
17	43	-37
19	53	-49
21	7*	-3
23	37	37
25	28	-31
27	33	-32
29	6*	3
31	13	11
33	17	19
H= -1, L= 3		
1	18	-13
3	32	-22
5	202	206
7	65	55
9	12	-4
11	34	-28
13	6*	6
15	39	44
17	68	74
19	54	-47
21	91	-90
23	42	-38
25	10	10
27	41	42
29	8	7
31	11	-13
33	14	-13
H= 2, L= 3		
2	142	-148
4	140	-143
6	209	196
8	181	175
10	158	148
12	17	16
14	82	-68
16	109	-93
18	64	66
20	12	-10
22	34	29
24	19	-19
26	32	-30
28	35	-31
30	7*	5
32	17	18
H= -2, L= 3		
2	128	133
4	18	20
6	6*	14
8	30	-24
10	52	-51
12	7*	5
14	56	48
16	8*	-1
18	27	-32
20	44	-46
22	9*	-4
24	9*	5
26	15	15
28	20	21
30	7*	5
32	5*	7
H= 3, L= 3		
1	31	-27
3	88	-79
5	5*	10
7	95	90
9	79	81
11	56	55
13	13	-13
15	84	-76
17	9*	-9
19	9*	8
21	9*	5
23	9	10
25	8*	-9
27	22	-21
29	7*	-1
31	5*	12
H= -3, L= 3		
1	68	-72
3	60	-65
5	29	28
7	28	27
9	44	42
11	17	13
13	56	-52
15	54	-54
17	26	-24
19	23	-19
21	9*	-11
23	9*	-2
25	8*	-2
27	8*	-14
29	7*	-2
31	6*	15
H= 4, L= 3		
2	94	96
4	49	49
6	57	-49
8	22	-23
10	45	-39
12	28	24
14	12*	6
16	35	-34
18	70	-62
20	13*	-4
22	32	-24
24	12*	3
26	12*	3
28	11*	6
30	10*	13
H= -4, L= 3		
2	171	-188
4	41	-61
6	40	41
8	96	101
10	64	53
12	47	-53
14	97	-94
16	43	-45
18	16	-12
20	19	17
22	12*	-10
24	12*	3
26	12*	-9
28	24	-25
30	10*	10
32	6*	24
H= 5, L= 3		
1	52	55
3	50	40
5	53	47
7	14	10
9	46	-38
11	51	-50
13	30	38
15	19	16
17	7*	-9
19	7*	-4
21	61	-55
23	40	-39
25	32	25
27	38	33
29	12	9
H= -5, L= 3		
1	27	-26
3	4*	8
5	20	-17
7	64	70
9	71	69
11	49	50
13	6*	5
15	6*	-1
17	27	-27
19	7*	4
21	26	22
23	14	15
25	6*	-1
27	31	-30
29	4*	-6
H= 6, L= 3		
2	26	24
4	48	41
6	20	11
8	48	-41
10	32	-31
12	8*	-4
14	8*	-4
16	8*	2
18	8*	-5
20	47	-43
22	36	-37
24	6*	-1
26	9	12
28	12	15
H= -6, L= 3		
2	5*	3
4	22	21
6	46	39
8	27	22
10	7*	4
12	8*	8
14	8*	12
16	8*	3
18	8*	-1
20	21	-20
22	26	-25
24	7*	0
26	5*	2
28	4*	-4
H= 7, L= 3		
1	10*	-13
3	45	52
5	16	16
7	20	21
9	51	48
11	70	72
13	19	18
15	11*	5
17	11*	-16
19	11*	4
21	20	22
23	12*	-2
25	12*	-7
27	12*	-18
H= -7, L= 3		
1	10*	0
3	30	29
5	22	21
7	21	22
9	16	-17
11	43	-41
13	11*	6
15	44	45
17	11*	7
19	11*	-8
21	30	-31
23	28	-29
25	30	26
27	30	25
H= 8, L= 3		
2	81	-86
4	11*	27
6	11*	9
8	26	19
10	87	87
12	11*	19
14	66	-55
16	29	-25
18	12*	-6
20	25	25
22	12*	12
24	12*	-1
26	31	-25
H= -8, L= 3		
2	30	23
4	50	50
6	11*	-13
8	11*	-7
10	18	-15
12	11*	2
14	18	16
16	29	29
18	32	-31
20	12*	-7
22	21	-23
24	12*	5
26	12*	4
H= 9, L= 3		
1	21	-30
3	21	-23
5	12*	-14
7	12*	10
9	32	34
11	12*	20
13	21	-27
15	23	-28
17	21	-23
19	12*	6
H= -9, L= 3		
1	12*	-10
3	12*	-10
5	12*	4
7	18	13
9	12*	9
11	12*	4
13	12*	-7
15	12*	-10
17	12*	-5
19	12*	2
H= 10, L= 3		
2	12*	15
4	12*	12
6	12*	1
8	12*	2
10	12*	11
12	12*	16
14	13*	-5
H=-10, L= 3		
2	35	-34
4	26	-21
6	19	19
8	22	19
10	26	23
12	12*	-1
14	12*	-26
H= 11, L= 3		
1	13*	15
3	25	27
5	13*	9
7	13*	-14
9	22	-26
H=-11, L= 3		
1	13*	-8
3	13*	-8
5	13*	-10
7	13*	6
9	13*	13
H= 0, L= 4		
0	38	26
2	41	33
4	23	20
6	44	-39
8	53	58
10	22	25
12	139	-126
14	109	-101
16	8*	-4
18	26	21
20	37	35
22	8*	-2
24	56	-55
26	8*	3
28	33	33
30	26	25
32	15	14
H= 1, L= 4		
1	38	44
3	66	69
5	34	34
7	57	49
9	12	-14
11	30	-32
13	24	-24
15	6*	3
17	14	-14
19	18	18
21	24	-20
23	7*	-2
25	14	14
27	15	13
29	6*	-1
31	5*	6
H= -1, L= 4		
1	28	-22
3	12	-4
5	64	58
7	44	45
9	12	8
11	95	-101
13	48	-48
15	7*	-12
17	32	35
19	28	23
21	32	30
23	33	-34
25	7*	-6
27	24	25
29	26	26
31	9	7
H= 2, L= 4		
0	28	33
2	64	69
4	83	-85
6	109	-109
8	14	-18
10	30	-24
12	7*	5
14	36	39
16	53	-50
18	36	-30
20	16	12
22	9*	7
24	53	50
26	38	37
28	8*	11
30	18	-12
32	4*	-11
H= -2, L= 4		
0	61	62
2	85	79
4	46	49
6	49	50
8	21	-24
10	22	-24
12	13	-11
14	8*	-9
16	31	-27
18	35	-34
20	28	-28
22	15	-15
24	16	14
26	8*	6
28	8*	-6
30	6*	-10
32	4*	3
H= 3, L= 4		
1	187	196
3	39	-40
5	146	-147
7	47	-51
9	7*	-5
11	85	90
13	40	41
15	70	-73
17	67	-58
19	20	19
21	14	-19
23	45	44
25	43	45
27	7*	7
29	6*	-7
31	4*	-6
H= -3, L= 4		
1	158	174
3	36	-38
5	64	-65
7	73	-73
9	7*	-8
11	71	79
13	13	22
15	55	-57
17	43	-45
19	35	-37
21	15	14
23	25	25
25	30	29
27	7*	8
29	15	-13
31	4*	-8
H= 4, L= 4		
0	45	38
2	30	20
4	33	-33
6	42	-42
8	39	-41
10	11*	6
12	11*	3
14	12*	-9
16	12*	-9
18	13*	-4
20	19	-18
22	18	19
24	31	32
26	22	20
28	11*	8
30	8*	-4
H= -4, L= 4		
0	197	217
2	49	-39
4	29	-31
6	12	-10
8	36	-39
10	26	-24
12	98	89
14	12*	-7
16	36	-23
18	34	-27
20	12*	-9
22	23	21
24	30	18
26	26	34
28	16	-9
30	8*	-14
H= 5, L= 4		
1	61	45
3	28	23
5	63	51
7	77	63
9	12	-16
11	50	-45
13	51	-42
15	42	-32
17	7*	-4
19	17	13
21	20	-21
23	32	-24
25	18	-11
27	4*	5
29	15	16
H= -5, L= 4		
1	14	-17
3	5*	-1
5	5*	15
7	31	-26
9	34	-36
11	16	-16
13	6*	-9
15	11	3
17	17	-1
19	16	-16
21	15	7
23	22	15
25	21	18
27	12	11
29	3*	3
H= 6, L= 4		
0	7*	-4
2	66	61
4	27	22
6	52	46
8	52	45
10	19	17
12	80	-69
14	65	-53
16	13	-11
18	42	40
20	12	14
24	23	-27
22	26	-30
26	18	-21
28	31	21
30	24	21
H= -6, L= 4		
0	20	-22
2	6*	-5
4	6*	8
6	26	27
8	7*	14
10	24	-23
12	31	-29
14	14	-15
16	8*	1
18	24	21
20	25	26
22	7*	-4
24	6*	-6
26	5*	-2
H= 7, L= 4		
1	26	-25
3	10*	-9
5	10*	5
7	10*	-0
9	10*	-11
11	29	-32
13	23	-29
15	11*	-5
17	12*	18
19	12*	11
21	12*	2
23	12*	-0
25	13*	2
27	13*	14
H= -7, L= 4		
1	19	-13
3	22	18
5	42	38
7	34	28
9	10*	9
11	51	-46
13	32	-26
15	11*	-5
17	11*	8
19	12*	2
21	12*	11
23	33	-27
25	12*	-17
H= 8, L= 4		
0	91	88
2	11*	7
4	11*	-6
6	20	-8
8	11*	-13
10	12*	-5
12	29	26
14	12*	-5
16	12*	-15
18	24	-20
20	12*	-4
22	13*	9
24	13*	11
26	25	24
H= -8, L= 4		
0	17	-3
2	11*	6
4	19	16
6	11*	9
8	11*	-9
10	11*	-10
12	12*	-6
14	12*	-1
16	12*	-4
18	12*	-7
20	12*	-2
H= 9, L= 4		
1	44	40
3	12*	-4
5	58	-56
7	52	-50
9	12*	7
11	36	35
13	13*	3
15	13*	-8
17	28	-25
19	18	-13
21	13*	7
23	23	17
25	23	21
H= -9, L= 4		
1	26	22
3	12*	9
5	23	-22
7	12*	-9
9	12*	-8
11	12*	8
13	27	23
15	12*	-1
17	28	-28
H= 10, L= 4		
0	25	28
2	13*	17
4	13*	-0
6	13*	-13
8	13*	-8
10	13*	3
H=-10, L= 4		
0	27	17
2	20	19
4	17	-15
6	20	-13
8	13*	-4
10	13*	-9
H= 0, L= 5		
2	84	-89
4	105	-97
6	63	64
8	15	14
10	42	41
12	7*	11
14	23	-21
16	31	-31
18	73	71
20	8*	1
22	47	44
24	7*	8
26	15	-18
28	31	-30
30	5*	-9
H= 1, L= 5		
1	46	-46
3	116	-116
5	27	-24
7	45	42
9	13	14
11	6*	0
13	13	-15
15	39	-35
17	36	35
19	39	32
21	19	17
23	31	26
25	9	5
27	24	-20
29	14	-14
31	4*	-3
H= -1, L= 5		
1	22	-20
3	30	-35
5	6*	-3
7	49	-47
9	37	-37
11	7*	3
13	28	-25
15	19	-17
17	25	24
19	7*	-6
21	7*	-1
23	27	25
25	7*	-9
27	13	-10
29	5*	-0
31	4*	-5
H= 2, L= 5		
2	15	15
4	6*	3
6	29	-28
8	7*	-4
10	33	-30
12	8*	10
14	8*	11
16	23	24
18	7*	3
20	23	19
22	13	-9
24	8*	7
26	7*	-5
28	7*	-5
30	5*	-5
H= -2, L= 5		
2	18	19
4	35	37
6	8*	2
8	61	-54
10	70	-65
12	12	-9
14	59	56
16	72	66
18	22	21
20	12	-15
22	13	-12
24	19	14
26	36	37
28	6*	10
30	11	-12
H= 3, L= 5		
1	52	62
3	38	40
5	7*	3
7	54	-64
9	102	-108
11	69	-75
13	51	54
15	52	46
17	11	12
19	14	14
21	28	-27
23	13	-9
25	35	38
27	23	28
29	5*	-3
H= -3, L= 5		
1	7*	5
3	7*	-3
5	59	62
7	34	-37
9	67	-70
11	46	-47
13	9*	12
15	41	40
17	54	57
19	20	-14
21	37	-42
23	8*	-10
25	11	15
27	21	26
29	5*	-2
31	23	-15
H= 4, L= 5		
2	12*	-1
4	20	15
6	20	-21
8	106	-103
10	100	-99
12	45	-44
14	15*	4
16	35	32
18	13	16
20	37	-46
22	30	-35
24	16	13
26	23	27
28	17	17
H= -4, L= 5		
2	25	23
4	25	-25
6	19	-20
8	25	-33
10	48	-50
12	21	-23
14	16*	10
16	11	11
18	10*	7
20	10*	-9
22	11*	5
24	10*	6
26	13	9
28	14	11
H= 5, L= 5		
1	23	-23
3	25	27
5	6*	-10
7	6*	-5
9	6*	-4
11	22	16
13	9	1
15	31	30
17	20	18
19	21	18
21	19	15
23	5*	-2
25	4*	7
27	3*	-4
H= -5, L= 5		
1	44	-40
3	39	-36
5	5*	2
7	29	-17
9	6*	2
11	6*	8
13	19	-16
15	12	-13
17	10	6
19	11	7
21	6*	11
23	13	11
25	5*	5
27	14	-15
H= 6, L= 5		
2	104	-78
4	33	31
6	35	-31
8	46	-45
10	56	50
12	28	20
14	41	-36
16	7*	-4
18	7*	3
20	31	31
22	24	26
24	14	16
26	13	-18
28	35	-24
H= -6, L= 5		
2	75	-76
4	22	-23
6	7*	3
8	29	30
10	26	25
12	17	-15
14	30	-29
16	8*	-5
18	8*	8
20	22	25
22	6*	3
24	5*	5
26	4*	-6
28	26	-20
H= 7, L= 5		
1	46	-47
3	43	-38
5	18	-13
7	7*	5
9	42	34
11	20	21
13	27	-26
15	8*	-12
17	9*	0
19	31	22
21	31	24
23	9*	11
25	10*	-5
27	20	-19
H= -7, L= 5		
1	21	-18
3	6*	-2
5	19	-17
7	6*	9
9	17	10
11	14	9
13	8*	-5
15	8*	7
17	8*	2
19	18	11
21	22	13
23	9*	8
25	9*	3
27	15	-11
H= 8, L= 5		
2	8*	-9
4	8*	-8
6	8*	-9
8	8*	-2
10	9*	4
12	9*	2
14	9*	-10
16	9*	6
18	9*	11
H= -8, L= 5		
2	12	14
4	12	14
6	8*	-3
8	28	-22
10	11	-20
12	8*	5
14	23	16
16	9*	9
18	9*	2
20	9*	-6
22	10*	-10
24	10*	6
26	10*	7
H= 9, L= 5		
1	24	20
3	37	36
5	9*	1
7	41	-41
9	53	-50
11	9*	-12
13	33	20
15	17	11
17	10*	-5
H= -9, L= 5		
1	9*	-2
3	20	15
5	9*	3
7	9*	-6
9	29	-19
11	23	-21
13	9*	1
15	29	23
17	9*	6
19	10*	1
21	17	-11
H= 10, L= 5		
2	30	32
4	24	24
6	10*	-4
8	19	-15
10	31	-24
12	10*	7
14	32	31
16	27	23
H=-10, L= 5		
2	9*	4
4	15	14
6	15	-12
8	13	-5
10	17	-9
12	10*	-3
H=-11, L= 5		
1	10*	-3
3	10*	-3
5	10*	-2
7	10*	-2
9	10*	-3
H= 0, L= 6		
0	7*	-10
2	21	23
4	48	-50
6	47	-48
8	20	21
10	15	18
12	17	17
14	30	30
16	26	-25
18	8*	-10
20	7*	10
22	7*	-9
24	7*	4
26	6*	-4
28	5*	-4
30	3*	-7
H= 1, L= 6		
1	30	30
3	42	-36
5	60	-58
7	6*	-8
9	6*	-6
11	59	58
13	65	62
15	7*	-1
17	20	-16
19	8*	10
21	30	-28
23	17	18
25	16	17
27	5*	-11
29	15	-19
H= -1, L= 6		
1	56	-55
3	11	7
5	34	32
7	51	45
9	14	8
11	7*	-9
13	7*	-9
15	30	27
17	27	22
19	28	25
21	16	-13
23	16	-16
25	19	-16
27	5*	-6
29	4*	-4
H= 2, L= 6		
0	23	-26
2	32	-35
4	61	-63
6	48	-47
8	26	-24
10	36	32
12	45	38
14	23	20
16	22	15
18	21	18
20	8*	-5
22	19	17
24	22	24
26	6*	5
28	5*	-4
30	3*	-6
H= -2, L= 6		
0	99	-92
2	43	-41
4	42	42
6	34	33
8	39	37
10	8*	-1
12	62	-58
14	20	-19
16	36	37
18	24	21
20	8*	10
22	14	-11
24	52	-49
26	14	-14
28	5*	8
30	3*	8
H= 3, L= 6		
1	8*	-9
3	32	-27
5	8*	-4
7	31	38
9	8*	15
11	9*	-0
13	9*	-11
15	8*	-10
17	8*	11
19	9*	23
21	8*	-9
23	17	-23
25	19	-23
27	5*	-9
H= -3, L= 6		
1	26	-30
3	18	-25
5	16	15
7	21	23
9	21	20
11	22	-17
13	9*	-1
15	9*	0
17	16	22
19	15	16
21	14	20
23	21	-23
25	18	-18
27	5*	-1
H= 4, L= 6		
0	91	-93
2	14*	-5
4	14*	20
6	63	68
8	54	49
10	15*	11
12	37	-45
14	16*	-10
16	33	30
18	53	57
20	14*	12
22	27	-35
24	24	-31
26	24	-29
H= -4, L= 6		
0	16	-18
2	14*	-1
4	15*	7
6	14*	11
8	15*	-11
10	15*	5
12	15*	19
14	16*	21
16	16*	7
18	15*	-11
20	14*	-13
22	13*	-4
24	11*	5
26	10*	-5
H= 5, L= 6		
1	54	-50
3	6*	-5
5	17	14
7	26	23
9	23	22
11	25	-23
13	33	-35
15	7*	3
17	33	32
19	20	17
21	5*	-8
23	24	-23
25	22	-25
H= -5, L= 6		
1	28	25
3	36	-33
5	13	-12
7	26	-26
9	11	-13
11	40	38
13	33	33
15	7*	-2
17	10	-9
19	23	-21
21	5*	6
23	5*	11
25	12	13
H= 6, L= 6		
0	72	55
2	28	-17
4	13	-15
6	8*	2
8	14	15
10	14	14
12	37	28
14	8*	-3
16	7*	1
18	6*	2
20	6*	2
22	5*	-5
24	3*	-13
H= -6, L= 6		
0	62	62
2	36	-34
4	25	-21
6	13	-12
8	8*	-10
10	8*	3
12	49	44
14	7*	2
16	8*	-2
18	12	-8
20	6*	4
22	5*	12
24	4*	-2
H= 0, L= 7		
2	7*	-9
4	7*	9
6	26	24
8	55	47
10	23	26
12	24	19
14	8*	-7
16	8*	2
18	8*	-10
20	7*	0
22	7*	-8
24	6*	1
26	13	-13
H= 1, L= 7		
1	38	41
3	38	39
5	27	28
7	7*	-3
9	26	-26
11	17	-13
13	40	43
15	17	16
17	13	-13
19	7*	-4
21	22	-23
23	6*	-8
25	16	19
27	10	13
H= -1, L= 7		
1	41	-43
3	88	-91
5	7*	5
7	82	77
9	55	53
11	17	9
13	31	-31
15	50	-48
17	8*	10
19	7*	9
21	7*	-5
23	10	5
25	5*	-4
27	13	-13
H= 2, L= 7		
2	14	-15
4	24	20
6	42	40
8	8*	-9
10	39	-38
12	29	-29
14	8*	-2
16	18	17
18	9*	4
20	50	-50
22	44	-45
24	6*	-1
26	15	18
28	3*	12
H= -2, L= 7		
2	27	-25
4	31	-26
6	37	37
8	9*	6
10	39	34
12	16	20
14	24	-20
16	36	-38
18	19	18
20	14	-15
22	20	23
24	7*	5
26	10	-12
28	11	-14
H= 3, L= 7		
1	15	-17
3	31	23
5	9*	7
7	9*	19
9	9*	3
11	8*	3
13	8*	-7
15	9*	15
17	9*	-2
19	8*	-11
21	7*	-10
23	6*	-8
25	5*	10
H= -3, L= 7		
1	9*	2
3	9*	0
5	14	16
7	9*	2
9	9*	1
11	9*	10
13	9*	-3
15	9*	-11
17	9*	1
19	16	-16
21	7*	-13
23	6*	6
25	5*	-6
H= 4, L= 7		
2	53	-56
4	44	36
6	16*	-6
8	16*	-16
10	41	48
12	16*	15
14	37	-39
16	14*	-22
18	23	-20
20	13*	7
22	11*	8
24	9*	10
H= -4, L= 7		
2	16*	-4
4	15*	17
6	17	26
8	16*	1
10	16*	-18
12	16*	-12
14	16*	11
16	15*	22
18	14*	7
20	13*	-20
22	11*	-21
24	9*	-1
H= 5, L= 7		
1	67	-56
3	54	-45
5	13	14
7	66	44
9	84	67
11	35	33
13	41	-31
15	22	-19
17	6*	-5
19	14	9
21	13	9
23	3*	3
H= -5, L= 7		
1	20	15
3	22	16
5	36	31
7	13	-12
9	24	-21
11	10	-5
13	17	15
15	6*	6
17	11	9
19	18	-15
21	24	-21
23	4*	-5
H= 6, L= 7		
2	24	-23
4	8*	-11
6	8*	9
8	27	27
10	22	22

TABLE II (*Continued*)

12	7*	-1
14	18	-19
16	11	-7
18	5*	-2
20	4*	5
22	3*	6
H= -6, L= 7		
2	8*	8
4	8*	-4
6	8*	4
8	7*	5
10	7*	1
12	8*	0
14	7*	-3
16	7*	-6
18	6*	-3
20	5*	-6
22	4*	1
H= 0, L= 8		
0	34	32
2	18	21
4	18	-20
6	39	-36
8	27	-30
10	8*	13
12	22	21
14	7*	0
16	15	-17
18	7*	-11
20	6*	-11
22	21	19
24	25	29
26	3*	9
H= 1, L= 8		
1	7*	10
3	7*	3
5	7*	-3
7	7*	2
9	7*	-9
11	7*	-10
13	7*	-7
15	7*	-6
17	7*	-7
19	7*	1
21	6*	-3
23	5*	4
25	4*	3
H= -1, L= 8		
1	44	40
3	8*	11
5	27	-24
7	17	-15
9	24	-13
11	23	19
13	25	24
15	8*	-10
17	28	-26
19	13	-6
21	14	-14
23	18	19
25	15	16
H= 2, L= 8		
0	34	-35
2	8*	16
4	8*	10
6	25	21
8	8*	11
10	8*	-3
12	33	-33
14	18	-15
16	8*	4
18	29	27
20	7*	12
22	6*	-8
24	5*	-1
H= -2, L= 8		
0	9*	4
2	32	28
4	9*	2
6	9*	-8
8	9*	1
10	9*	-10
12	9*	-6
14	9*	9
16	19	-18
18	17	-13
20	7*	-3
22	6*	-3
24	5*	8
26	3*	3
H= 3, L= 8		
1	8*	-10
3	25	26
5	8*	16
7	8*	7
9	9*	9
11	25	-26
13	38	-39
15	8*	-10
17	8*	8
19	7*	4
21	6*	-4
23	5*	-8
H= -3, L= 8		
1	9*	-9
3	16	15
5	14	14
7	9*	8
9	9*	-4
11	9*	-10
13	17	-18
15	8*	1
17	8*	3
19	7*	8
21	6*	0
23	5*	1
H= 4, L= 8		
0	43	44
2	16*	0
4	16*	8
6	15*	8
8	15*	4
10	14*	-7
12	14*	4
14	14*	-9
16	13*	0
18	12*	-3
20	11*	-3
22	8*	-2
H= -4, L= 8		
0	18	-25
2	16*	-8
4	18	26
6	16*	16
8	16*	5
10	15*	-9
12	17	-28
14	15*	-12
16	13*	14
18	12*	4
20	10*	3
22	9*	2
H= 5, L= 8		
1	42	31
3	7*	6
5	51	-40
7	52	-40
9	6*	7
11	26	22
13	6*	-6
15	5*	-6
17	21	-18
19	14	-12
21	6	5
H= -5, L= 8		
1	6*	0
3	6*	-0
5	17	11
7	6*	2
9	6*	-3
11	19	-12
13	6*	-1
15	5*	-3
17	5*	1
19	4*	-3
21	4*	9
H= 6, L= 8		
0	58	50
2	38	33
4	7*	-8
6	32	-29
8	7*	-21
10	17	17
12	17	16
14	6*	-4
16	19	-21
18	15	-21
H= -6, L= 8		
0	13	12
2	13	10
4	8*	-1
6	13	-10
8	13	-12
10	7*	6
12	7*	10
14	6*	3
16	6*	-6
18	5*	-12
H= 0, L= 9		
2	8*	8
4	11	15
6	8*	7
8	29	-26
10	31	-30
12	7*	-5
14	17	17
16	24	21
18	12	11
20	17	-19
22	15	-18
H= 1, L= 9		
1	7*	-8
3	7*	14
5	8*	-3
7	7*	-7
9	31	-24
11	18	-17
13	7*	-2
15	25	24
17	13	12
19	6*	-2
21	4*	-7
23	3*	-2
H= -1, L= 9		
1	8*	10
3	8*	5
5	8*	5
7	8*	-6
9	17	-17
11	16	-13
13	15	14
15	15	11
17	10	6
19	9	9
21	5*	-7
H= 2, L= 9		
2	40	-38
4	9*	12
6	13	-10
8	17	-19
10	12	8
12	8*	-5
14	16	-18
16	7*	3
18	7*	-1
20	6*	7
22	4*	-1
H= -2, L= 9		
2	9*	-11
4	9*	-6
6	9*	-3
8	9*	4
10	9*	1
12	8*	3
14	8*	-5
16	7*	6
18	6*	3
20	6*	6
22	5*	5
H= 3, L= 9		
1	32	-34
3	24	-23
5	9*	0
7	8*	-3
9	8*	16
11	8*	13
13	8*	-15
15	7*	-2
17	6*	3
19	6*	9
21	4*	12
H= -3, L= 9		
1	9*	-13
3	33	-35
5	9*	-5
7	9*	13
9	8*	6
11	8*	3
13	8*	-9
15	18	-21
17	6*	6
19	5*	8
21	4*	2
H= 4, L= 9		
2	14*	-26
4	14*	-19
6	14*	-4
8	14*	8
10	13*	1
12	13*	-13
14	12*	-12
16	11*	5
18	9*	6
H= -4, L= 9		
2	15*	-12
4	15*	-16
6	15*	9
8	14*	-8
10	14*	4
12	13*	4
14	12*	-9
16	11*	-10
18	9*	17
20	7*	-5
H= 5, L= 9		
1	6*	-4
3	6*	4
5	6*	4
7	8	-8
9	17	-14
11	7	-5
13	5*	2
15	9	5
17	3*	5
H= -5, L= 9		
1	6*	8
3	6*	7
5	6*	3
7	16	-11
9	14	-12
11	5*	-1
13	9	5
15	5*	4
17	4*	5
H= 6, L= 9		
2	25	25
4	16	16
6	6*	-6
8	13	-14
10	26	-26
12	4*	2
14	20	29
H= -6, L= 9		
2	7*	3
4	7*	8
6	7*	3
8	6*	-11
10	11	-12
12	6*	-3
14	5*	7
H= 0, L= 10		
0	31	-29
2	7*	-1
4	7*	-3
6	7*	4
8	7*	9
10	6*	6
12	6*	-10
14	6*	-3
16	5*	3
18	13	16
H= 1, L= 10		
1	34	-34
3	14	12
5	20	18
7	14	11
9	7*	5
11	13	-16
13	6*	-14
15	5*	9
17	11	15
H= -1, L= 10		
1	7*	-9
3	7*	-0
5	7*	-2
7	7*	2
9	7*	-1
11	6*	1
13	6*	6
15	5*	6
17	5*	-1
19	4*	-1
H= 2, L= 10		
0	8*	-6
2	20	-16
4	7*	7
6	7*	12
8	8*	7
10	7*	-5
12	7*	1
14	6*	1
16	6*	11
18	4*	6
H= -2, L= 10		
0	8*	-4
2	8*	3
4	8*	-1
6	8*	-7
8	8*	-11
10	8*	5
12	14	13
14	6*	9
16	6*	-2
18	5*	-5
20	3*	-11
H= 3, L= 10		
1	7*	6
3	7*	-2
5	13	-20
7	13	-16
9	7*	12
11	12	18
13	6*	-2
15	5*	0
17	4*	-4
H= -3, L= 10		
1	8*	8
3	8*	1
5	8*	-15
7	8*	-5
9	7*	2
11	7*	12
13	6*	12
15	5*	-3
17	4*	-9
19	3*	1
H= 4, L= 10		
0	12*	5
2	12*	6
4	12*	-3
6	12*	-13
8	11*	-5
10	11*	12
12	10*	14
14	8*	8
H= -4, L= 10		
0	13*	-15
2	13*	1
4	13*	2
6	13*	3
8	12*	3
10	11*	-4
12	10*	-3
14	9*	8
16	7*	-0
H= 5, L= 10		
1	5*	-4
3	5*	-2
5	4*	-1
7	4*	-8
9	4*	8
11	3*	3
H= -5, L= 10		
1	19	-17
3	5*	4
5	15	12
7	5*	6
9	5*	-2
11	4*	-5
13	6	-7
H= 6, L= 10		
0	4*	-6
2	9	-10
4	4*	3
6	3*	0
H= -6, L= 10		
0	5*	-8
2	5*	-6
4	5*	5
6	5*	4
8	5*	3
H= 0, L= 11		
2	6*	-13
4	6*	10
6	6*	1
8	5*	-1
10	5*	8
12	4*	1
H= 1, L= 11		
1	18	-17
3	5*	-9
5	5*	4
7	5*	2
9	12	14
11	5*	11
H= -1, L= 11		
1	6*	-3
3	6*	7
5	6*	2
7	6*	6
9	5*	-2
11	4*	-5
13	4*	-3
H= 2, L= 11		
2	17	-19
4	9	-11
6	6*	6
8	17	19
10	5*	11
12	5*	-8
H= -2, L= 11		
2	7*	8
4	7*	9
6	6*	5
8	6*	-6
10	5*	-7
12	5*	3
14	4*	7
H= 3, L= 11		
1	6*	-6
3	5*	-2
5	5*	4
7	5*	5
9	5*	4
11	4*	3
H= -3, L= 11		
1	6*	3
3	6*	1
5	6*	3
7	6*	1
9	5*	-0
11	5*	0
13	3*	4
H= 4, L= 11		
2	8*	11
4	8*	8
6	7*	1
H= -4, L= 11		
2	10*	-8
4	10*	-5
6	9*	2
8	8*	4
10	7*	6
H= -5, L= 11		
1	3*	-2
3	9	-9

TABLE III

DISTANCES (Å) AND ANGLES (DEG)[a]

Ti–O(7)	1.825 (2)	O(7)–Ti–O(5)	100.8 (4)
O(5)	1.872 (7)	O(7)–Ti–O(6)	100.5 (4)
O(6)	1.905 (7)	O(7)–Ti–O(3)	95.4 (2)
O(3)	2.072 (6)	O(7)–Ti–O(4)	91.7 (2)
O(4)	2.074 (6)	O(7)–Ti–N	90.4 (4)
N	2.172 (7)	O(7)–Ti–O(8)	170.5 (3)
O(8)	2.183 (7)	O(8)–Ti–N	80.3 (3)
O(7)–O(4)	2.803 (7)	O(8)–Ti–O(5)	87.3 (3)
N	2.846 (10)	O(8)–Ti–O(3)	83.3 (3)
O(5)	2.849 (9)	O(8)–Ti–O(4)	83.9 (3)
O(6)	2.870 (9)	O(8)–Ti–O(6)	88.7 (3)
O(3)	2.888 (6)	O(5)–Ti–O(6)	45.2 (4)
O(8)–N	2.81 (1)	O(5)–Ti–O(3)	127.4 (3)
O(5)	2.81 (1)	O(5)–Ti–O(4)	85.8 (3)
O(3)	2.83 (1)	O(5)–Ti–N	155.6 (4)
O(4)	2.85 (1)	O(6)–Ti–O(3)	82.8 (3)
O(6)	2.86 (1)	O(6)–Ti–O(4)	130.9 (3)
O(5)–O(6)	1.45 (1)	O(6)–Ti–N	153.6 (3)
O(4)	2.69 (1)	O(3)–Ti–O(4)	143.5 (3)
O(3)–O(6)	2.63 (1)	O(3)–Ti–N	72.1 (3)
O(8)–O(9)	2.71 (1)	O(4)–Ti–N	72.1 (3)
O(8)–O(1″)	2.74 (1)	Ti–O(7)–Ti	178.1 (8)
O(9)–O(2″)	2.71 (1)	Ti–O(3)–C(1)	124.2 (6)
K(1)–O(6)	2.808 (8)	Ti–O(4)–C(7)	121.7 (5)
O(5)	2.856 (8)	Ti–N–C(2)	118.7 (5)
O(4′)	2.881 (6)	Ti–N–C(6)	118.9 (5)
O(5′)	3.122 (9)	Ti–O(5)–O(6)	68.6 (4)
O(9′)	3.273 (10)	Ti–O(6)–O(5)	66.2 (4)
O(7)	3.297 (10)	O(1″)–O(8)–O(9)	109.5 (4)
K(2)–O(3)	2.81 (1)	Ti–O(8)–O(9)	121.0 (4)
O(5‴)	2.84 (1)	Ti–O(8)–O(1″)	119.6 (4)
O(6)	2.88 (1)	O(8)–O(9)–O(2″)	118.9 (4)
O(6‴)	2.91 (1)	C(7)–O(2)–O(9″)	114.3 (6)
O(8″)	3.16 (1)	C(1)–O(1)–O(8″)	116.8 (6)
O(8‴)	3.31 (1)		
O(6″)	3.43 (1)		
O(9′)	3.64 (1)		

[a] Symmetry positions: $-x, -y, -z(')$; $-x, y, -z('')$; $x, -y, +z(''')$. The standard errors are indicated in parentheses. For the distances and angles in the dipicolinic acid see Figures 2 and 3.

TABLE IV

LEAST-SQUARES PLANES

Plane	Coeff[a]	Atoms comprising the plane	Displacements, Å
1	−0.7902	Ti	−0.08
	−0.0331	O(3)	0.06
	0.6120	O(4)	0.06
	0.498	N	−0.03
2	−0.7974	Ti	0.0
	−0.2165	O(5)	0.0
	0.5633	O(6)	0.0
	2.870		
3	−0.7498	N	0.005
	−0.0530	C(1)	−0.013
	0.6596	C(2)	0.002
	0.444	C(3)	0.025
		C(4)	−0.010
		C(5)	−0.007
		C(6)	−0.016
		C(7)	0.014
	−0.7167	C(1)	−0.021
	−0.0109	C(2)	0.006
	0.6973	O(1)	0.008
	−0.079	O(3)	0.007
5	−0.6699	C(7)	0.015
	−0.1884	C(6)	−0.004
	0.7181	O(2)	−0.006
	1.084	O(4)	−0.005
6	0.5932	O(8)	0.008
	0.0	Ti	−0.018
	0.8051	O(7)	0.0
	−4.531	Ti″	0.018
		O(8″)	−0.008

[a] These are coefficients for the equation of the plane in the form $AX + BY + CZ + D = 0$, with X, Y, Z in ångströms measured along a, b, c^*.

TABLE V

ANGLES BETWEEN LEAST-SQUARES PLANES

Planes	Angle, deg	Planes	Angle, deg
1–2	10.9	2–6	91.1
1–3	3.8	3–4	3.8
1–6	88.6	3–5	9.6

through various groups of atoms[18] are presented in Table IV; the angles between these planes, in Table V.

As expected, the two titanium atoms are connected by the oxygen O(7) that lies on the twofold axis. The angle Ti–O(7)–Ti of 178.1 ± 0.8° is not significantly different from 180°. The peroxy groups O(5) and O(6), rather than having the bridging configuration, are attached symmetrically, "laterally," to each titanium atom separately. Similar to many other transition

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[18] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12**, 600 (1959).

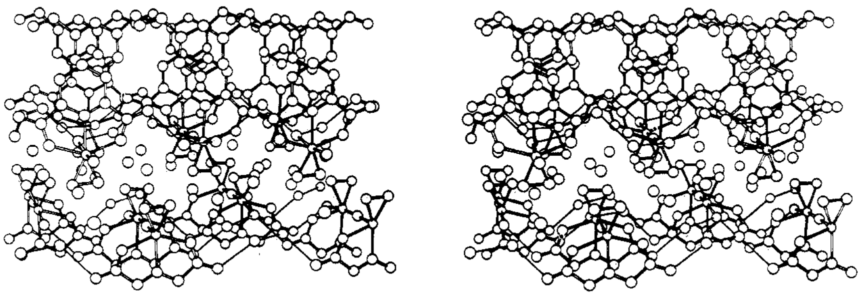
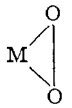


Figure 4.—Stereoscopic view of the structure. The bonds drawn as single lines are hydrogen bonds. The spheres without bonds are potassium ions. The planes of the dipicolinic acid ligands are parallel to $(10\bar{1})$.

metal peroxides,[9] the titanium is heptacoordinated in a distorted pentagonal bipyramid. Three of the corners of the pentagon are occupied by the dipicolinic acid with angles N–Ti–O(3) and N–Ti–O(4) of 72.1 ± 0.3°, and the other two are occupied by the peroxy group. The pentagon is distorted mainly because of the short O(5)–O(6) distance. The water O(8) and the oxygen bridge O(7) sit on the apices of the bipyramid. The nonchelated binuclear peroxytitanium complex may therefore be assumed to have the composition $[\mathrm{Ti(O_2)}\cdot 4\mathrm{H_2O}]_2\mathrm{O}^{2+}$. The coordination polyhedron could alternatively be described by a distorted octahedron with the peroxy group occupying one coordination position as a monodentate ligand.

The distance Ti–O(7) is very short (1.825 ± 0.002 Å) but it agrees well with the corresponding distance found in a binuclear acetylacetonate complex of Ti(IV).[19] The distances Ti–O(5) (1.872 ± 0.007 Å) and Ti–O(6) (1.905 ± 0.007 Å) are shorter than the Ti–O distances of 1.944 ± 0.004 and 1.988 ± 0.006 Å in rutile,[20] in contrast to the distances Ti–O(3) (2.072 ± 0.006) Å, Ti–O(4) (2.074 ± 0.006 Å), Ti–N (2.172 ± 0.007 Å), and Ti–O(8) (2.182 ± 0.007 Å). The difference between the distances Ti–O(5) and Ti–O(6) of 0.033 ± 0.010 Å is not significantly different from zero. The O(5)–O(6) distance of $1.45_3 \pm 0.01_2$ Å in the peroxy group is equal to the distance of 1.453 ± 0.007 Å found by Busing and Levy[6] in H_2O_2. The O(5)–Ti–O(6) angle of 45.2 ± 0.4° is normal for



arrangements. The plane defined by Ti and the three coordinating atoms of the dipicolinic acid Ti–N–O(3)–O(4), as well as the plane defined by Ti and the peroxy group Ti–O(5)–O(6), while enclosing an angle of 10.9°, are both nearly perpendicular to the plane defined by the long axis of the complex and the twofold axis O(8)–Ti–O(7)–Ti″–O(8″) (88.6 and 91.1°). The peroxy dumbbell is therefore moved out of the plane Ti–N–O(3)–O(4) toward O(8), while remaining parallel to it. The distances between O(7) and its nearest neighbors N, O(3), O(4), O(5), and O(6), as well as between these atoms and O(8), are all in the range of 2.8–2.9 Å, suggesting that the geometry of the complex is strongly influenced by steric factors. The peroxy group seems to be pushed out of the plane Ti–N–O(3)–O(4) by the bridging atom O(7) as a result of the short Ti–O(7) distance. O(8) appears to be pushed toward N by the peroxy group, resulting in an O(8)–Ti–N angle of 80.3 ± 0.3°.

The large deviations of the angles O(3)–Ti–N and O(4)–Ti–N from 90° are due to the position of the peroxy group. In addition to the distortion of the angles N–C(2)–C(1) (111 ± 0.7°), N–C(6)–C(7) (111 ± 0.6°), C(2)–C(1)–O(3) (114 ± 0.8°), and C(6)–C(7)–O(4) (114 ± 0.7°) from 120°, the carboxyl groups of the dipicolinic acid are forced out of the plane of the pyridine ring by 3.8 and 9.6°, turning the pyridine ring by 3.8° relative to the plane Ti–N–O(3)–O(4). The contacts O(3)–O(6), 2.63 ± 0.01 Å, and O(4)–O(5), 2.69 ± 0.01 Å, are still very short. The dimensions of the dipicolinic acid molecule are normal. The biggest difference between the lengths of chemically equivalent bonds, N–C(2) and N–C(6), is $0.04_6 \pm 0.01_6$ Å.

It is difficult to decide how the metal–peroxide bonding should be described. The peroxy group is "laterally" coordinated to the metal in most of the peroxy complexes of transition metals whose structures are known, usually leading to a distorted pentagonal arrangement with the dumbbell in the plane of the pentagon. It seems to behave as a monodentate ligand.[9,21,22] The bonding has been described as a donation of electrons to the metal ion from the π-bonding and the π^*-antibonding orbitals of the peroxy group. On the other hand, it is possible that the peroxy group may be bound by two σ bonds to the titanium, *i.e.*, that the titanium is participating in seven distinct electron pair bonds. Stomberg[22] noted a small but significant difference between the two distances from the metal to the peroxy group in chromium peroxides. However, the difference between Ti–O(5) and Ti–O(6) in this structure is not large enough to be significant. Seven- and eight-coordinated titanium has been previously prepared with the compact ligands tropolone[23] and nitrate[24] where again the π orbitals of the ligand may be involved in the metal–ligand bonding.

(19) K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **6**, 963 (1967).

(20) W. H. Baur, *Acta Crystallogr.*, **9**, 515 (1956).

(21) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

(22) R. Stomberg, *Acta Chem. Scand.*, **22**, 1439 (1968).

(23) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **87**, 4706 (1965).

(24) C. D. Garner and S. C. Wallwork, *J. Chem. Soc. A*, 1496 (1966).

A stereoscopic view of the packing of the complexes is shown in Figure 4. The complexes are arranged in layers perpendicular to *b* with all the peroxy groups on one side and the pyridine rings on the other. The distances between O(8) and O(1″) of the neighboring complex (2.74 ± 0.01 Å), between O(8) and the uncoordinated water molecule O(9) (2.71 ± 0.01 Å), and between O(2) and O(9) (2.71 ± 0.01 Å) are in the range to suggest hydrogen bonding, and the angles around O(1), O(2), O(8), and O(9) support this evidence. The hydrogen-bonded layers are stacked in such a way that alternatively either their peroxy sides or their pyridine sides face each other. The potassium ions are in the holes between layers the peroxy sides of which point at each other. K(1), the ion sitting on the twofold axis, is in a cavity with six nearest oxygen neighbors at 2.81–2.88 Å and five more oxygen neighbors at 3.12–3.30 Å. However, the disordered ion K(2) occupying a general eightfold position with half occupancy is rather irregularly surrounded by eight oxygens, the K(2)–O distances ranging uniformly from 2.81 to 3.64 Å. The large temperature factors for this ion and the residual electron density found on its fringes in the final difference-Fourier map suggest that the ion is sitting in a hole too large for its size and may be disordered in the hole.

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The Crystal and Molecular Structure of Tris(ethylenediamine)cobalt Pentacyanonitrosylchromate Dihydrate, $[Co(C_2H_8N_2)_3][Cr(CN)_5(NO)] \cdot 2H_2O$

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The structure of tris(ethylenediamine)cobalt pentacyanonitrosylchromate dihydrate $[Co(C_2H_8N_2)_3][Cr(CN)_5(NO)] \cdot 2H_2O$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The material crystallizes in the space group C_{2h}^5-$P2_1/c$ with four molecules in a cell of dimensions a = 13.47 (2), b = 11.59 (1), c = 13.39 (2) Å, and β = 100.5 (1)°. Both the observed and calculated densities are 1.58 g cm^{-3}. Least-squares refinement of the structure has led to a final value of the conventional R factor of 0.053 for the 1106 observed data having $F^2 \geq 3\sigma(F^2)$. The structure consists of discrete $Co(C_2H_8N_2)_3^{3+}$ cations and $Cr(CN)_5(NO)^{3-}$ anions. A network of hydrogen bonds connects the cations, anions, and water molecules. The $Cr(CN)_5(NO)^{3-}$ anion is ordered, and the NO ligand is unambiguously distinguished from the CN ligands. The symmetry of the anion is nearly $4mm$-C_{4v}. The Cr–N distance is 1.71 (1) Å and the N–O distance is 1.21 (1) Å. The Cr–N–O angle is 176 (1)°. The average equatorial Cr–C distance is 2.033 (7) Å, and the axial Cr–C distance is 2.075 (14) Å; the average C–N distance is 1.158 (7) Å. The Co atom of the cation has the expected trigonally distorted octahedral coordination environment. For a Λ configuration of the cation the conformation of the complex is $\Delta\partial\lambda\lambda$.

Introduction

In recent years there has been considerable interest in the molecular and electronic structure of transition metal pentacyanonitrosyls of the general formula $M(CN)_5(NO)^{n-}$. An X-ray structure determination[2] showed that the nitroprusside anion, $Fe(CN)_5(NO)^{2-}$, has approximate $4mm$-C_{4v} symmetry. The electronic and electron spin resonance (esr) spectra of several other pentacyanonitrosyl anions were subsequently interpreted[3] on the basis of C_{4v} symmetry, and a general molecular orbital bonding scheme was proposed for the anions. Of particular interest to us was the $Cr(CN)_5(NO)^{3-}$ anion. Although the anion was assumed to have C_{4v} symmetry for the molecular orbital calculations, the esr spectrum of the anion shows an anisotropic ^{14}N hyperfine splitting. McGarvey and Pearlman[4] have interpreted this as indicative of a nonlinear Cr–N–O moiety. Other workers have also postulated a bent Cr–N–O linkage[5] but subsequently reinterpreted[6] their data as favoring linear attachment of the NO group. An X-ray structure determination[7] has been reported for $K_3Cr(CN)_5(NO)$. Unfortunately the crystal structure is disordered so that the CN and NO ligands are statistically distributed about the six coordination positions. Although the Cr–N–O group appeared linear, such might not be the case. Moreover, the disorder precluded obtaining accurate Cr–N and N–O distances.

In order to establish conclusively the coordination geometry of the $Cr(CN)_5(NO)^{3-}$ anion in an ordered

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