Table 10 (*cont.*)

L	4·00	0·4203	−0·8085	−0·4119
	3·59	0·1769	0·5184	−0·8366
	3·27	0·8900	0·2790	0·3606

Displacements of the libration axes from the origin (0,0,0) in Å, referred to the directions of the principal axes of **L**. Screw pitches of the libration axes in Å(°)$^{-1}$.

	Displacement along axis			
Axis	1	2	3	Screw pitch
1		−1·55	2·86	0·0043
2	−1·60		2·95	−0·0098
3	−1·15	−1·63		0·0052

The standard deviations of the r.m.s. amplitudes are 0·003 Å for **T** and 0·25° for **L**.

Table 10 describes the results in terms of three translations and three screw librations about three non-intersecting axes. Of the three screw pitches, only two are independent. The ones listed are derived by setting the trace of S equal to zero. T and L are not very different from the tensors listed in Table 7, and the screw pitches are quite small. However, the three libration axes do not intersect. The axes 2 and 3 are displaced by 0·45 Å parallel to axis 1.

The author wishes to thank Dr R. J. Stedman for supplying the crystals, and Professor G. A. Jeffrey for his continued interest in the work and help in preparing the manuscript.

The work was supported, in part, by grant number DA-ARO-D-31-124-G786, from the U.S. Army Research Office, Durham.

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The Crystal Structure of Decammine-μ-peroxo-dicobalt Pentanitrate*

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(*Received* 23 *February* 1967)

The structure of decammine-μ-peroxo-dicobalt pentanitrate, $(NH_3)_5CoO_2Co(NH_3)_5(NO_3)_5$, has been re-examined. The substance forms tetragonal crystals, $a=11\cdot96$, $c=8\cdot08$ Å; there are two formula units in the cell. We have collected a completely new set of data and, working in space group $P4_2/mnm$, we have refined the structure to an R index of 0·054 for 361 non-zero reflections. Every atom in the structure, except the cobalt atoms, appears to suffer some degree of disorder; for some of the nitrate groups this disorder is so severe as to prevent a satisfactory description of them. However, the detailed structure of the cation is clear: each cobalt atom is bonded to only one of the oxygen atoms of the bridging $-O_2-$ group, and the O–O axis is skewed to the Co–Co axis, just as was found in the salt $(NH_3)_5CoO_2Co(NH_3)_5SO_4(HSO_4)_3$. The O–O distance and the planarity of the Co–O–O–Co atoms both indicate that the bridging group is a superoxide radical, rather than a peroxide ion.

Introduction

The crystal structure of decammine-μ-peroxo-dicobalt pentanitrate, $(NH_3)_5CoO_2Co(NH_3)_5(NO_3)_5$, was first investigated by Vannerberg & Brosset (1963; hereafter VB). They derived a structure, based on the space group $P4_2nm$, in which the bridging peroxide group was perpendicular to the Co–Co direction (I); this arrangement had been proposed earlier on theoretical grounds by Vlček (1960). On the other hand, we have found a skewed arrangement (II) for the cation $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ crystallized as the monosulfate tris(bisulfate) salt (Schaefer & Marsh, 1966). We

* Contribution no. 3482 from the Gates and Crellin Laboratories of Chemistry. This work was supported by Grant GP-5768 from the National Science Foundation.

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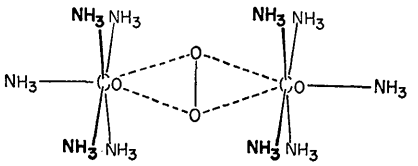
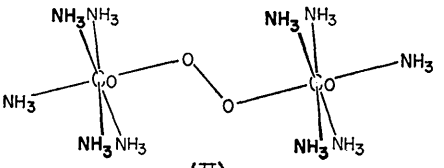
thought it surprising that the same cation should have two such radically different structures, and accordingly we have reinvestigated the structure of the pentanitrate compound. We report here the results. While rather severe disorder has limited the accuracy of this reinvestigation, especially in regard to the arrangement of the nitrate anions, it is clear that the cation has the skew arrangement (II), rather than the more symmetric arrangement (I) proposed by VB.



(I)



(II)

Experimental

The compound was prepared by the method of Gleu & Rehm (1938), but with nitrate salts substituted for sulfate everywhere. The impure product was twice recrystallized from dilute (2:100) nitric acid (Werner & Mylius, 1898); the second recrystallization took place overnight in a stoppered Dewar flask. The resulting crystals were of several habits; needles elongated along **c** and small prisms with principal faces (001) predominated. Preliminary Weissenberg photographs of a needle-shaped crystal indicated a tetragonal unit cell with dimensions close to the values reported by VB. A comparison of these photographs with the ones prepared by VB (and kindly sent to us by Prof. Vannerberg) showed them to be closely similar but not identical; the most prominent discrepancy involved the 200 reflection which was missing on the photographs of VB but was of moderate intensity on ours. We believe that these discrepancies are associated with the severe structural disorder in this compound (see later *Discussion*), and reflect variations in the perfection of the crystals, or perhaps the water content, rather than fundamental differences in the molecular structure.

Unit-cell dimensions were obtained from a zero-level Weissenberg photograph of a prismatic crystal rotated about its [110] axis, prepared with copper radiation and a special camera that holds the film in the asymmetric position. The crystal data are given in Table 1, together with the values found by VB. The Laue symmetry $4/mmm$ and the absence of reflections $0kl$ with $k+l$ odd indicate the possible space groups $P4_2nm$, $P4n2$ or $P4_2/mnm$ as previously noted by VB.*

Table 1. *Crystal data for decammine-μ-peroxo-dicobalt pentanitrate*

$Co_2O_{17}N_{15}H_{30}$ Mol. wt. = 630·20
Probable space group: $P4_2/mnm$ $Z=2$ $F(000)=650$
%Cobalt: calc., 18·71; found, 18·74.

	This work	Vannerberg & Brosset (1963)
a =	11·961 (4) Å	11·94 (2) Å
c =	8·078 (1)	8·06 (1)
d_m =	1·827 g.cm^{-3}	1·840 g.cm^{-3}
d_x =	1·811*	1·821 g.cm^{-3}

Cu $K\alpha_1$ = 1·54051 Å
Cu $K\alpha_2$ = 1·54433
Cu $K\alpha$ = 1·5418

* Loss of weight on drying in a vacuum desiccator over phosphorus pentoxide corresponded to about 0·35 mole of water per mole of compound. The density calculated on the basis of 0·7 molecules of water per unit cell is 1·829 g.cm^{-3}, in almost exact agreement with the experimental value, and thus it is probable that our crystals contain a small amount of water. This water undoubtedly participates in the disorder.

Intensity data were collected on a General Electric diffractometer automated by Datex, using MnO_2-filtered iron radiation and a proportional counter. A θ–2θ scan technique was used, the scan range including both the α_1 and α_2 peaks; background was counted for 100 seconds at each end of the scan, and the scanning rate was 1° per minute in 2θ. The crystal used was an irregularly shaped prism with maximum dimensions 0·175 × 0·087 × 0·145 mm, mounted along the [110] axis. Three sets of data were collected, two sets coming from the same portion of the reciprocal lattice (to test the reliability of the apparatus) and the third set coming from a portion of the reciprocal lattice rotated 90° in the a^*b^* plane from the other two. The three sets agreed very well, nearly within the counting statistics. A single reflection (440) was checked periodically during the entire data collection process; its variation also was comparable with the variation noted among the three sets of data.

To obtain a single set of observed structure factors and their standard deviations, we first corrected all the measured intensities for background and then applied Lorentz and polarization corrections. No correction for absorption was considered necessary, since μR_{max} is less than 1; moreover, the sets of data collected from the two different orientations of the crystal showed no

* No reflections $0kl$ with $(k+l)$ odd were visible on our photographs or on those of VB. However, of the 43 reflections of this type surveyed on the diffractometer, 12 were measured slightly but significantly greater than zero. Although double reflection may be partly responsible, the possibility remains that the net glide and the diagonal symmetry planes are not truly present. In light of the disordered over-all structure that we have found, it is easy to imagine that, in some small domains, an ordering exists which might lead to the space group $P4_2/m$ for these domains. The resulting differences in intensity between reflections hkl and khl would be undetectably small.

discernible effect due to absorption. The three resulting structure amplitudes were then averaged; if this average was negative it was set equal to zero.

The standard deviations assigned to the intensities were calculated from the equation

$$\sigma^2(I) = S + (B_1 + B_2)\alpha^2 + (dS)^2$$

(Peterson & Levy, 1957).

Here, S is the scan count, B_1 and B_2 are the background counts, d is an empirical constant, determined as described later, and $\alpha = n/2mt$ where n = scan range, m = scanning speed, and t = time for the background count (100 seconds). The constant d was chosen by considering the relative agreement among the three sets of data collected; the number obtained was 0·017. Approximately the same number has been found by other people in this Laboratory using the same equipment; it presumably reflects experimental errors other than counting statistics, such as current and voltage fluctuations.

Derivation and refinement of the structure

The structure derived by VB was based on the space group $P4_2nm$; however, deviations from the centrosymmetric space group $P4_2/mnm$ were quite small and associated primarily with some of the nitrate groups. Our initial calculations were a set of structure factors based on VB's parameters for the cobalt atom, and a three-dimensional electron-density map; since only the cobalt atoms were used, this map had the symmetry of space group $P4_2/mnm$.

The electron-density map indicated that the general arrangement of atoms proposed by VB was approximately correct; however, a number of disturbing features were apparent. These included: (*a*) obvious disorder of the nitrate group at $\frac{1}{2}$,0,0, as noted by VB; (*b*) probable disorder of the bridging O_2 groups; these atoms were not resolved and the area between the cobalt atoms appeared only as a region of approximately constant electron density; (*c*) diffuse, nonspherical peaks at the positions of all the NH_3 groups, suggesting either disorder or large, anisotropic temperature factors. These difficulties could not be obviated by assuming either of the non-centrosymmetric space groups $P4_2nm$ or $P\bar{4}n2$, and accordingly refinement was initiated in the space group $P4_2/mnm$.

Although a few cycles of least-squares calculations were carried out, refinement was primarily by means of difference maps. The reason for this choice was that, in order to represent the disorder, we found it necessary in several instances to place pairs of atoms at very nearly the same positions; this led to near-singularities in the least-squares normal equations. All calculations were carried out on an IBM 7094 computer under the CRYRM crystallographic computing system (Duchamp, 1964). Form factors for Co, N, and O were taken from *International Tables for X-ray Crystallography* (1962), the values for cobalt being reduced by 1·8 electrons to take account of anomalous dispersion. Form factors for hydrogen were taken from Stewart, Simpson & Davidson (1965).

As refinement progressed, it became apparent that we were not going to be able to obtain completely satisfactory agreement between the observed and calculated structure factors without assuming so complicated a pattern of disorder and thermal motion that the number of parameters would approach the number

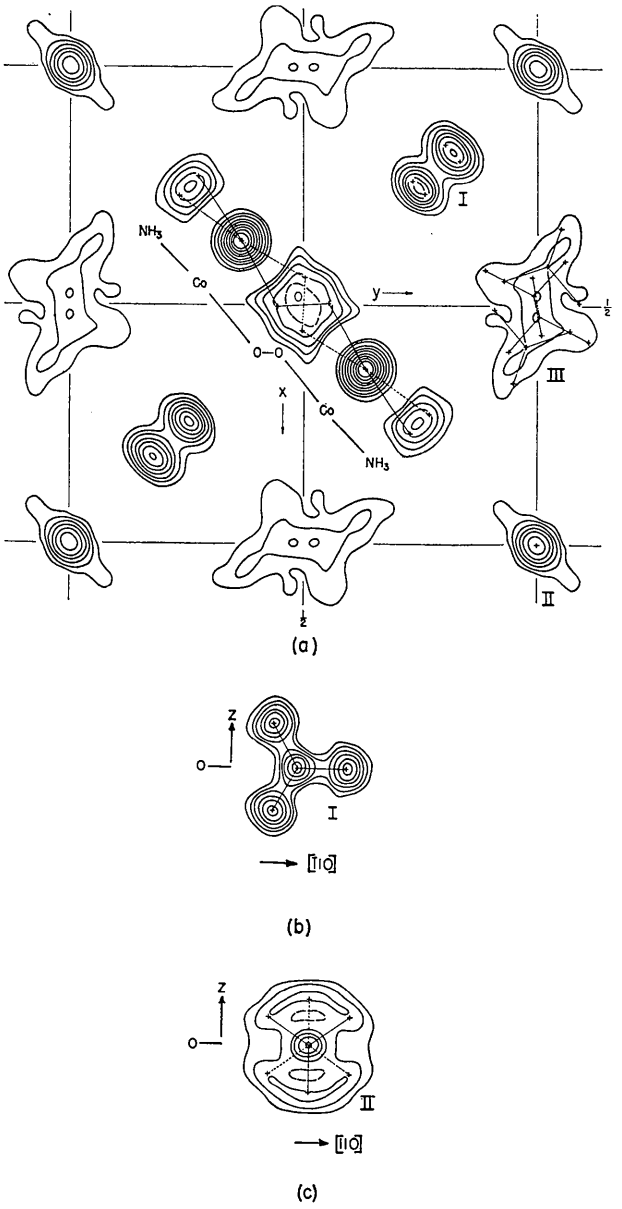


Fig. 1. Electron density maps calculated at the conclusion of the refinement. (*a*) The section $z=0$. (*b*) A section parallel to (110), through nitrate group I. (*c*) A section parallel to $(1\bar{1}0)$, through nitrate group II. Contours are at 1, 2, 3... e.Å^{-3} except around the cobalt atoms, where they are at 1, 5, 10, 15... e.Å^{-3}. Crosses indicate the final atomic positions. All heavy atoms in the structure are shown except for the nitrogen atoms N(1) and N(2), which complete the octahedra about the cobalt atoms.

of observations. Similarly, although disorder in one of the nitrate groups (that centered at $\frac{1}{2},\frac{1}{2},0$) might have been removed by assuming the lower-symmetry space group $P4_2nm$, disorder of the other groups would have remained and the introduction of the additional parameters (and phase angles) seemed unwarranted. Accordingly, the structure we report is based on space group $P4_2/mnm$.

The electron-density map shown in Fig. 1, which was calculated at the end of the refinement, illustrates most of the difficulties associated with the disorder. No matter which of the three possible space groups is selected, the two diagonal directions [1,1,0] and [$\bar{1}$,1,0] in the section $z=0$ [Fig. 1(*a*)] must be either twofold axes or lie in mirror planes, and a twofold axis parallel to **c** must pass through the points ($\frac{1}{2}$,0) and (0,$\frac{1}{2}$). Thus for any choice of space group we are forced to position a nitrate group near, and perpendicular to, a twofold axis (which is impossible in an ordered structure) and to give a twofold disorder to the cation. This we have done, to the best of our ability, in the space group of highest symmetry.

The final parameters are listed in Table 2. For the atoms of nitrate group III (Fig. 1), they were obtained from difference maps; the hydrogen atoms were also positioned with the help of difference maps, but constrained so that the N–H distances are 1·0 Å and the H–N–H angles 105°. The parameters of the Co, N, and O atoms of the cation and of nitrate groups I and II were adjusted by four full-matrix least-squares calculations carried out after the positions of the remaining atoms had been fixed. The quantity minimized was $\Sigma\, w(F_2^0-F_c^2)^2$, where weights w were taken equal to $(1/\sigma^2)F_0^2$ (see *Experimental*); six strong reflections were assigned weights of zero. In the final least-squares cycle, no parameter shifted by as much as 10% of its standard deviation.

The final value of the 'goodness of fit', $[\Sigma w(F_0^2-F_c^2)^2/(m-s)]^{\frac{1}{2}}$, is 9·0, a clear indication that the model does not adequately explain the data. The trouble almost certainly is due to the disorder, which not only gives rise to considerable uncertainty as to the arrangements of nitrate groups II and III but also raises the possibility of short-range order which the conventional method of calculating structure factors does not take into account. (We carried out one structure-factor calculation on the basis of long-range order, assuming a twinning of crystals having the symmetry of the orthorhombic space group *Pnnm*; this model was clearly incorrect. Since the disorder is very complicated, we did not think it fruitful to investigate all the possible patterns of short-range order.)

Observed and calculated structure factors are listed in Table 3. The final R index ($R=\Sigma\,(F_o-|F_c|)/\Sigma\, F_o$)

Table 2. *The final atomic parameters*

For the Co, N, and O atoms of the cation and of nitrate groups I and II the parameters were obtained from least-squares calculations and the standard deviations are given in parentheses; parameters of the remaining atoms were obtained from difference maps and no standard deviations are given. The columns labelled M and F give the number of atoms of each kind in the cell and the fractional occupancy of the sites. Anisotropic temperature factors are given in the form $\exp[-(\beta(11)h^2+\beta(22)k^2+\beta(33)l^2+\beta(12)hk+\beta(13)hl+\beta(23)kl)]$.

		M	F	x	y	z	$\beta(11)$ or B	$\beta(22)$	$\beta(33)$	$\beta(12)$	$\beta(13)$	$\beta(23)$
Cation	Co	4	1	0·1343 (1)	x	0	0·0033 (1)	$\beta(11)$	0·0067 (3)	−0·0008 (2)	0	0
	O	4	$\frac{1}{2}$	−0·0028 (7)	0·0550 (7)	0	2·6 (2)					
	N(1)	8	$\frac{1}{2}$	0·1988 (10)	0·0397 (10)	0·1711 (14)	2·7 (3)					
	N(2)	8	$\frac{1}{2}$	0·0640 (10)	0·2282 (10)	0·1709 (14)	2·6 (3)					
	N(3)	4	$\frac{1}{2}$	0·2680 (9)	0·2283 (9)	0	2·5 (3)					
Nitrate group I	N	4	$\frac{1}{2}$	0·7698 (9)	0·2606 (9)	0	1·9 (2)					
	O	8	$\frac{1}{2}$	0·8075 (6)	0·2256 (6)	0·1341 (8)	3·1 (2)					
	O	4	$\frac{1}{2}$	0·6948 (9)	0·3341 (10)	0	3·0 (2)					
Nitrate group II	N	2	1	$\frac{1}{2}$	$\frac{1}{2}$	0	0·009 (2)	$\beta(11)$	0·006 (4)	0·013 (4)	0	0
	O	2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	−0·139 (3)	0·016 (3)	$\beta(11)$	0·010 (6)	0·020 (6)	0	0
	O	4	$\frac{1}{2}$	0·438 (1)	x	0·087 (3)	0·013 (1)	$\beta(11)$	0·032 (4)	−0·003 (3)	0·018 (4)	$\beta(13)$
Nitrate group III	N	2	$\frac{1}{8}$	−0·022	0·493	0·020	3·0					
	O	2	$\frac{1}{8}$	−0·075	0·390	0·050	4·0					
	O	2	$\frac{1}{8}$	0·060	0·510	0·040	6·0					
	O	2	$\frac{1}{8}$	−0·096	0·560	0·020	6·0					
	N	2	$\frac{1}{8}$	0·085	0·478	0·030	6·0					
	O	2	$\frac{1}{8}$	0·164	0·450	0·030	6·0					
	O	2	$\frac{1}{8}$	0·007	0·410	0·030	6·0					
	O	2	$\frac{1}{8}$	0·054	0·571	0·040	6·0					
N(1)	H	8	$\frac{1}{2}$	0·217	0·079	0·277	5·0					
	H	8	$\frac{1}{2}$	0·273	0·004	0·138	5·0					
	H	8	$\frac{1}{2}$	0·152	−0·026	0·204	5·0					
N(2)	H	8	$\frac{1}{2}$	0·081	0·205	0·286	5·0					
	H	8	$\frac{1}{2}$	0·085	0·309	0·165	5·0					
	H	8	$\frac{1}{2}$	−0·020	0·228	0·165	5·0					
N(3)	H	8	$\frac{1}{2}$	0·275	0·279	0·098	5·0					
	H	4	$\frac{1}{2}$	0·341	0·184	0	5·0					

for 361 reflections of non-zero weight is 0·054. A difference map calculated at the conclusion of the refinement showed no excursions larger than 0·5 e.Å^{-3}.

It is cogent to point out that the F(cal) value for the 200 reflection, which is in rather severe disagreement with our value of F(obs), agrees well with the observation of VB (on whose photographs this reflection could not be seen). The 200 reflection is particularly sensitive to the arrangement of the nitrate groups at $0,\frac{1}{2},0$ and $\frac{1}{2},\frac{1}{2},0$, and hence to the details of the disorder; furthermore, since the remaining discrepancies between our photographs and those of VB are very small, it is apparent that the structure we have derived is in good accord with VB's data. Accordingly, our conviction is firm that the same general structure – and, in particular, the geometry of the cation – obtains in all crystals of this compound.

Table 3. *Observed structure factors, their standard deviations, and the final calculated structure factors* (*all* × 10)

Asterisks in the column of standard deviations indicate reflections assigned zero weight in the final least-squares calculations.

H 0 0			H 2 1			H 4 2			H 7 3		
2	81	1 -7	2	755	4 -772	4	800	4 818	7	123	1 119
4	580	3 555	3	174	1 -160	5	180	1 -187	8	100	1 107
6	67	1 -36	4	215	1 -216	6	247	2 -256			
8	199	2 209	5	7	9 -6	7	34	3 -20		H 0 4	
10	186	2 -178	6	600	3 567	8	176	2 -177	0	910	5 971
12	204	1 -202	7	13	10 0	9	29	6 7	2	112	1 142
			8	208	2 -200	10	114	1 120	4	520	3 -480
H 1 0			9	87	2 -95				6	185	2 169
1	553	** 668	10	302	2 -291		H 5 2		8	450	3 453
2	799	** -877	11	26	5 38	5	114	2 116	10	182	1 -180
3	582	3 -594				6	210	2 -202			
4	139	1 -152		H 3 1		7	112	2 -100		H 1 4	
5	396	2 377	3	20	4 -29	8	91	2 92	1	116	1 69
6	495	3 512	4	406	2 392	9	78	2 -74	2	670	3 -631
7	219	2 175	5	326	2 317	10	214	1 224	3	301	2 -311
8	294	2 -291	6	66	2 -67				4	476	3 453
9	125	2 125	7	57	2 41		H 6 2		5	181	2 -176
10	159	2 -152	8	398	2 -386	6	140	2 143	6	226	2 217
11	223	2 -251	9	191	2 -184	7	104	2 -111	7	361	2 363
			10	185	1 192	8	34	5 -16	8	65	2 -54
H 2 0			11	22	5 -27	9	272	2 259	9	24	6 18
2	1010	** 1094				10	21	3 -16	10	148	1 -162
3	410	2 -407		H 4 1							
4	93	1 -1	4	213	1 186		H 7 2			H 2 4	
5	515	3 527	5	356	2 337	7	123	1 141	2	392	2 413
6	223	1 197	6	382	2 -369	8	69	2 76	3	263	2 -251
7	31	3 36	7	544	3 -639	9	109	1 113	4	66	2 46
8	38	3 30	8	149	2 135				5	391	2 397
9	362	2 -354	9	179	2 -177		H 8 2		6	129	2 94
10	146	1 160	10	62	2 49	8	261	2 251	7	87	2 83
11	36	2 -28	11	194	1 207				8	124	1 -120
							H 0 3		9	252	2 -264
H 3 0			H 5 1			1	62	1 79	10	83	1 87
3	705	** 779	5	517	3 -486	3	136	1 -141			
4	977	6 1011	6	318	2 -292	5	670	3 -643		H 3 4	
5	281	2 259	7	169	2 -166	7	736	4 728	3	432	2 418
6	305	2 286	8	281	2 -259	9	72	2 74	4	170	1 -155
7	325	2 -296	9	339	2 335	11	237	1 -223	5	248	2 249
8	178	2 154	10	37	2 24				6	295	2 314
9	33	6 -15					H 1 3		7	364	2 -374
10	270	2 -271		H 6 1		1	408	2 -367	8	147	1 -146
11	223	1 230	6	475	3 -471	2	572	3 519	9	29	4 -15
			7	79	2 65	3	44	2 -22	10	122	1 -112
H 4 0			8	107	2 106	4	504	3 -463			
4	1035	6 1080	9	27	5 -30	5	511	3 495		H 4 4	
5	138	2 -130	10	187	1 178	6	166	1 156	4	530	3 554
6	251	2 -274				7	224	2 230	5	116	2 -145
7	149	2 154		H 7 1		8	317	2 321	6	244	2 -245
8	394	2 -384	7	44	3 -31	9	208	2 -217	7	28	6 -36
9	125	2 139	8	195	1 196	10	153	1 -155	8	135	1 -136
10	169	1 164	9	102	1 104	11	80	1 -90	9	13	7 -2
11	41	2 -36									
				H 8 1			H 2 3			H 5 4	
H 5 0			8	37	2 -55	2	488	3 -494	5	33	6 -38
5	334	2 357				3	217	1 215	6	273	2 -278
6	372	3 -394		H 0 2		4	118	1 107	7	40	3 -38
7	292	2 -278	0	2315	** 2218	5	128	1 128	8	81	1 80
8	256	2 271	2	267	1 257	6	635	3 623	9	123	1 -125
9	141	1 -133	4	436	3 -399	7	132	2 -122			
10	202	1 198	6	196	1 179	8	142	2 -117		H 6 4	
			8	485	3 503	9	195	2 -191	6	136	1 140
H 6 0			10	200	2 -183	10	252	2 -241	7	124	1 -122
6	269	2 243				11	15	3 4	8	64	1 -53
7	208	2 -206		H 1 2							
8	82	2 85	1	35	1 -7		H 3 3			H 7 4	
9	294	2 280	2	535	3 -515	3	608	3 -581	7	72	1 66
10	32	3 -13	3	318	2 -307	4	591	3 568			
			4	562	3 540	5	267	2 261		H 0 5	
H 7 0			5	213	1 -200	6	92	2 -80	1	556	3 554
7	432	3 452	6	553	3 565	7	57	3 67	3	200	2 -199
8	78	2 75	7	448	2 454	8	375	2 -373	5	267	2 -244
9	111	1 133	8	159	2 -162	9	256	2 -249	7	235	2 242
			9	31	6 8	10	103	1 90	9	33	2 45
H 8 0			10	178	1 -180						
8	269	2 244	11	147	1 -151		H 4 3			H 1 5	
						4	270	2 -270	1	378	2 -349
				H 2 2		5	147	1 140	2	83	2 68
H 0 1			2	1232	** 1350	6	38	3 -34	3	233	2 -235
1	740	4 744	3	393	2 -390	7	331	2 -340	4	214	2 -192
3	820	4 -784	4	66	1 -49	8	143	2 -147	5	179	2 162
5	102	1 -124	5	538	3 637	9	83	1 -74	6	40	3 38
7	283	2 254	6	103	2 56	10	148	1 140	7	73	2 81
9	151	2 156	7	112	2 99				8	154	1 151
11	390	2 -390	8	135	2 -144				9	170	1 -189
			9	338	2 -338		H 5 3				
			10	48	2 51	5	133	2 -130		H 2 5	
H 1 1			11	25	4 -20	6	182	2 -140	2	467	3 -420
1	213	1 -201				7	156	2 -152	3	131	2 -111
2	317	2 -306		H 3 2		8	61	2 -48	4	110	2 111
3	760	4 -767	3	824	4 834	9	308	2 295	5	164	2 141
4	279	2 -275	4	34	2 -33	10	51	2 54	6	322	2 330
5	172	1 214	5	191	1 194				7	106	1 -98
6	75	1 83	6	399	2 399				8	101	1 -98
7	144	1 150	7	394	2 -385		H 6 3		9	34	2 -13
8	313	2 332	8	113	2 -134	6	258	2 -234			
9	360	2 -362	9	86	2 -80	7	29	6 26		H 3 5	
10	119	2 -119	10	147	1 -138	8	186	1 173	3	113	2 -40
11	13	8 -13	11	139	1 136	9	24	2 -25	4	363	2 351

5	275	2 265									
6	73	2 -74									
7	128	1 129									
8	284	2 -281									
9	163	2 -163									
	H 4 5										
4	144	2 148									
5	148	1 154									
6	58	2 -60									
7	377	2 -381									
8	50	1 48									
	H 5 5										
5	221	2 -239									
6	154	1 -132									
7	141	1 -136									
8	136	1 -133									
	H 6 5										
6	365	2 -363									
7	102	1 94									
	H 0 6										
0	1154	6 1213									
2	147	2 -138									
4	45	3 -24									
6	99	1 104									
8	220	1 230									
	H 1 6										
1	300	2 314									
2	444	2 -435									
3	222	2 -225									
4	27	6 2									
5	77	2 66									
6	145	1 138									
7	157	1 151									
8	129	1 -124									
	H 2 6										
2	140	2 149									
3	224	2 -223									
4	54	2 54									
5	244	2 245									
6	128	1 129									
7	50	2 44									
	H 3 6										
3	296	2 297									
4	187	2 186									
5	189	1 182									
6	129	1 134									
7	198	1 -203									
	H 4 6										
4	474	3 484									
5	89	2 -82									
6	150	1 -150									
7	60	1 62									
	H 5 6										
5	106	1 110									
6	264	2 -271									
	H 0 7										
1	281	2 292									
3	306	2 -308									
5	94	1 -102									
	H 1 7										
1	40	3 -62									
2	74	2 -60									
3	254	2 -256									
4	169	1 -171									
5	163	1 160									
6	13	5 -7									
	H 2 7										
2	271	2 -253									
3	---	** 10									
4	22	5 24									
5	54	1 -52									
	H 3 7										
3	23	5 -16									
4	156	1 159									
5	144	1 138									
	H 4 7										
4	106	1 132									
	H 0 8										
0	476	3 465									
2	111	1 -120									
	H 1 8										
1	167	1 196									

Description of the structure

The cation

Interatomic distances and angles within the cation are listed in Table 4, together with the corresponding values found in the sulfate-tris(bisulfate) salt (Schaefer & Marsh, 1966). The agreement between the two sets of bond distances and angles is excellent – perhaps even better than the estimated standard deviations might predict. Accordingly, the same valence-bond description that was invoked for the sulfate-tris(bisulfate) compound seems appropriate here; the Co–O bonds are single bonds and the O–O bond is a single bond plus a 3-electron bond, and thus the bridging radical is a superoxo group. The unpaired spin should lie almost entirely on this O_2 group.

Table 4. *Interatomic distances and bond angles within the decammine-μ-peroxo-dicobalt cation in this compound* (*a*) *and in the monosulfate tris(bisulfate) compound* (*b*) (*Schaefer & Marsh*, 1966)

Only the structurally distinct values in the present investigation are given; since the cation in (*b*) has no crystallographic symmetry, many values in that column are averages of two or four distinct measurements. Standard deviations in both investigations are about 0·003 Å for the Co···Co distances, 0·01–0·02 Å for the remaining distances, and 1–2° for the bond angles.

	(*a*)	(*b*)
O—O	1·317 Å	1·312 Å
Co–O	1·895	1·894
Co–N(1)	1·946	1·950
Co–N(2)	1·968	1·937
Co–N(3)	1·955	1·958
Co···Co	4·545	4·562
Co—O—O′	117·3°	117·6°
N(1)–Co–O	93·0	92·8
N(2)–Co–O	85·2	86·3
N(3)–Co–O	174·9	177·2
N(2)–Co–N(1)	90·2	89·9
N(3)–Co–N(1)	90·6	89·1
N(3)–Co–N(2)	91·2	91·8
N(1)–Co–N(1′)	90·6	91·7
N(2)–Co–N(2′)	89·1	88·6
N(2)–Co–N(1′)	178·1	177·9

In both compounds the O–O bond is staggered with respect to the adjacent Co–N(1) bonds, and the non-bonded Co···Co distance is further lengthened by a slight bending of the Co–O bond away from the octahedral direction.

The slightly anisotropic motion of the cobalt atom, as implied by the temperature parameters in Table 2, may represent a small displacement associated with the disorder of the cation.

The nitrate groups

The final parameters of nitrate group I (Fig. 1), which were obtained by least-squares refinement, correspond within experimental error (about 0·02 Å) to a plane trigonal group with an average N–O distance of 1·25 Å. The isotropic temperature factors of the

atoms in this group are also reasonable, being somewhat larger for the oxygen atoms than for the nitrogen atom.

The situation in regard to the other two nitrate groups is considerably less satisfactory. Whereas for group I, as well as for the cation, the disorder generates pairs of atoms which are separated from one another by 0·45 Å or more in all cases, the disorder associated with groups II and III seems to generate a larger number of atoms (each with lower population), and in any event leads to an electron-density distribution in which the individual atoms cannot be resolved (Fig. 1). In these cases, we have tried to fit the electron density with as small a number of parameters as possible; and while the resulting atomic arrangements bear some formal relationship to nitrate groups, the bond distances and angles are hardly reasonable.

Nitrate group II we have represented by twofold disorder of anisotropically vibrating atoms – a total of 13 parameters. The resulting temperature factors are rather unreasonable, in that they correspond to a very large in-plane translational motion along [110] (suggesting additional disorder); the bond distances are 1·13 and 1·27 (twice) Å, and the angles 123 (twice) and 113°.

Nitrate group III is represented by eightfold disorder of isotropic atoms. Here, the slight displacement of the atoms from the mirror plane $z=0$, which was clearly dictated by the appearance of the difference maps, may indicate either a small tilting of the groups or out-of-plane vibrations; the large distance between successive groups (which are stacked on top of one another, along the c axis, with a separation of $c/2$, or 4·0 Å) permits either explanation. However, our representation is clearly incomplete, for the bond distances between the N and O atoms identified as in Table 2 range from 1·00 to 1·41 Å and the angles from 105 to 128°.

If a small amount of water is present, as is indicated by drying over phosphorus pentoxide as well as by the measured density, structural considerations suggest that the sites of the water molecules are near – and probably obscured by – the regions of electron density assigned to nitrate group III. The amount of water estimated to be present corresponds to an occupancy factor of less than 10% for a site of type $x,y,0$, or less than 5% for a general site x,y,z.

The hydrogen bonding

In view of the disorder, we are unable to discuss the hydrogen bonding in any detail. Each of the nitrogen atoms of the cation has three or more oxygen atoms of neighboring nitrate groups at reasonable distances (3·1 Å or less) and in satisfactory directions to account for all the possible hydrogen bonds; however, which of the disordered oxygen atoms accepts a particular hydrogen bond is unclear. The hydrogen bonding almost surely introduces a cooperative effect between the disordering of the cation and of the nitrate groups, which may well lead to a good deal of short-range order in the structure, but we are unable to deduce the details of this effect or any super-structure which might arise from it.

We are indebted to Professor Vannerberg for the original photographs prepared by VB, as well as for encouragement and stimulation.

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