hydrogen bonds. The assignment of hydrogen bonds to observed short N–O contacts can be made with the help of the hydrogen positions. In Table 4(*a*), five N–O contacts which are within hydrogen bond distances are listed together with the angles around the hydrogen atoms. The contact III with a relatively sharp N–H–O angle can be eliminated as a hydrogen bond; therefore contacts I and II are considered as the hydrogen bonds formed by H(5) and H(6), respectively. For H(7), there are two choices, IV and V; although the configuration around the nitrogen atoms [Table 4 (*b*)] seems to favor contact IV as the hydrogen bond formed by H(7), the evidence is not strong enough to preclude the fifth (intramolecular) contact as a possible one. It is also possible to consider that H(7) is actually involved in a bifurcated hydrogen bond system with these two contacts. In either case, O(3) is involved in two hydrogen bonds; this is rather interesting because the S–O(1) and S–O(3) bond lengths are almost the same, although O(1) is involved in only one hydrogen bond. A similar situation was found in the structure of D-tartaric acid, where the two carboxyl groups in the molecule exhibit almost equal C=O distances, although one of these two double bonded oxygen atoms receives two hydrogen bonds whereas the other receives only one (Okaya, Stemple & Kay, 1966). As discussed before, O(2) with a short S–O bond is not involved in hydrogen bond formation. Fig. 6 shows drawings of the structure viewed down the *a* and *c* axes. The hydrogen bond system is illustrated in the drawings by shaded lines.

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The Structure of Decammine-μ-peroxo-dicobalt Monosulfate Tris(bisulfate)*

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Decammine-μ-peroxo-dicobalt monosulfate tris(bisulfate), $(NH_3)_5CoO_2Co(NH_3)_5SO_4(HSO_4)_3$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a=16{\cdot}36$, $b=13{\cdot}95$, and $c=9{\cdot}98$ Å; there are four formula units in the cell. The structure was determined by Patterson and trial-and-error methods and refined by three-dimensional least-squares calculations based on 1458 reflections. The final R index is 0·078 and the standard deviations in the coordinates are about 0·003, 0·005, 0·02, and 0·02 Å for the Co, S, N, and O atoms.

The coordinating ligands about the cobalt atoms form nearly regular octahedra with Co–N and Co–O distances of 1·95 and 1·89 Å. The Co–O–O–Co group is planar, with the bridging peroxide group skewed to the Co–Co axis; the O–O distance is 1·31 Å and the Co–O–O angles are 118°. The ions are held together by a very extensive network of hydrogen bonds which appears to involve all 33 hydrogen atoms.

Recently Vannerberg & Brosset (VB; 1963) have reported the results of a crystal-structure investigation of the bridged dicobalt compound decammine-μ-peroxo-dicobalt pentanitrate,

$$(NH_3)_5CoO_2Co(NH_3)_5(NO_3)_5\ .$$

They reported the O–O axis of the bridging peroxide group to be perpendicular to the Co–Co axis, a configuration in agreement with that postulated earlier by Vlček (1960) for the decammine-μ-peroxo-dicobalt(5+) cation; this configuration could result, according to Vlček, from overlap of cobalt *d*-orbitals with π-electrons on the bridging O_2 group. However, VB's results were based on a relatively small number of observed reflections and their final R index was

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rather high (0·20); moreover, the space group that they found required that at least some of the atoms in the nitrate groups be disordered.

In view of our doubts concerning the reasonableness of the model proposed by Vlček, we have investigated the crystal structure of another salt containing the same decammine-μ-peroxo-dicobalt cation. This salt turned out to be decammine-μ-peroxo-dicobalt monosulfate tris(bisulfate), $(NH_3)_5CoO_2Co(NH_3)_5SO_4(HSO_4)_3$. A preliminary report of this work has been published (Schaefer & Marsh, 1966).

Experimental

Decammine-μ-peroxo-dicobalt disulfate bisulfate trihydrate, $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2HSO_4.3H_2O$, was prepared by the method of Gleu & Rehm (1938). The impure product was crystallized from $2F$ sulfuric acid rather than $2N$, the concentration used by Gleu & Rehm; this difference in procedure was to cause confusion later. Crystallization yielded dark green crystals in three habits: needles elongated along **c**, thin plates with principal faces (100), and small, nearly cubic parallelepipeds. Weissenberg photographs of the $hk0$ and $h0l$ zones showed all of these kinds of crystal to be orthorhombic with space group $P2_12_12_1$ (systematic absences $h00$, $0k0$, and $00l$ with h, k, or l odd). For unit-cell measurements, Weissenberg photographs of these same zones were taken in a special camera which holds the film in the asymmetric position; the crystals used were a needle, about 0·2 mm in diameter, mounted along **c** and a plate mounted along **b** and ground to an approximate cylinder 0·4 mm in diameter. The crystal data, including the density as measured by flotation in carbon tetrachloride–bromoform solution, are given in Table 1.

Table 1. *Crystal data for decammine-μ-peroxo-dicobalt monosulfate tris(bisulfate)*

$a = 16{\cdot}360 \pm 1$ Å	$Co_2N_{10}H_{33}O_{18}S_4$
$b = 13{\cdot}946 \pm 3$	M.W. 707·5
$c = 9{\cdot}978 \pm 1$	$Z = 4$
Space group $P2_12_12_1$	$F(000) = 1460$
$D_m = 2{\cdot}060 \pm 0{\cdot}005$ g.cm^{-3}	$D_x = 2{\cdot}064$ g.cm^{-3}

$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051$ Å
$\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54433$
$\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$

Assuming four molecules in the unit cell, the density calculated for the parent compound

$$(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2HSO_4.3H_2O\,,$$

which we supposed we had prepared, is 1·94 g.cm^{-3}, far below the observed value. Subsequently, during our attempts to interpret c-axis electron density projections, it appeared likely that instead of three sulfate groups in the formula unit there were four. Accordingly, a new batch of the compound was prepared and analyzed for cobalt (by precipitating and weighing $K_3Co(NO_2)_6$; Lingane, 1964) and for sulfur (by precipitating and weighing $BaSO_4$). The resulting composition was Co, 16·65% and S, 17·7%, giving a Co:S ratio of 2·00:3·91 ± 0·02. For the formula

$$(NH_3)_5CoO_2Co(NH_3)_5SO_4(HSO_4)_3$$

we calculate a density of 2·064 g.cm^{-3} and the composition Co, 16·66% and S, 18·13%. We therefore have taken this to be the formula of the compound; it was later confirmed by our structure analysis.

We have also prepared the compound described by Gleu & Rehm (1938),

$$(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2HSO_4.3H_2O\,,$$

by crystallizing the impure compound from $1F\,H_2SO_4$. It forms dark green monoclinic needles (probable space group $P2_1/c$); its structure is presently under investigation in these laboratories. This material also was analyzed for Co and S by the same procedures and the resulting Co:S ratio was 2·00:2·99. The close agreement of these results with the theoretical values strengthens our confidence in the analytical procedures and our belief that there is a real, though small, deficiency of sulfate in the orthorhombic crystals. Careful measurement of the density of a large number of crystals from the original batch showed them to be homogeneous and ruled out the possibility that our analyses were carried out on a mixture of the two compounds: however, a difference map calculated at the end of the refinement showed no significant negative regions. It is possible that the missing material was removed as sulphuric acid from the surface of the crystals during washing.

Zero-level data around the c axis were collected with copper radiation. These pictures were somewhat darkened because of cobalt fluorescence, but were quite usable for obtaining intensities. However, after about 50 or so hours of radiation it was evident that the crystal was slowly decomposing in the beam; therefore, the rest of the data were collected with the use of iron radiation. Intensities were estimated visually from multiple-film Weissenberg photographs of layer lines 0–7 about **c** and of the zero layer about **b**; in all, 1458 intensities were recorded, of which 101 were below the observational threshold. Even with iron radiation, the intensities of high-angle reflections diminished after 100–200 hours of exposure, and therefore in preparing intensity photographs no crystal was exposed to X-rays for more than 100 hours.

Initial data processing included assignment of an estimated standard deviation to each individual observation (see Sharma & McConnell, 1965), correction for absorption, Lorentz and polarization factors, and the scaling together of the different observations to give a value of F^2 and $\sigma(F^2)$ for each independent reflection. (The spots on the $hk7$ and $h0l$ photographs were poorly formed, and the values of $[\sigma(F^2)]^2$ of these observations were doubled.) These standard deviations were the basis for the weights used in the final cycles of least-squares refinement. The absorption corrections were made assuming that all the crystals, whose cross-sections were actually almost square, were cylinders 0·2 mm in diameter. In view of the large number of crystals used in collecting the data, no more sophisticated corrections seemed warranted. The primary purpose of the correction was to permit the *hk*0 data obtained with copper and iron radiations to be scaled together, since for this compound there is a relatively large difference in the mass absorption coefficients (119 for Fe and 167 for Cu).

Determination and refinement of the structure

Although this compound contains a relatively small number of heavy atoms, and although there are a number of obvious clues to the structure (such as the weakness of the odd layer lines about **c**, requiring that many pairs of atoms be separated by about $\frac{1}{2}$ in *z*, and the great strength of the 230 and 400 reflections, suggesting a hexagonal arrangement of the heavy atoms in projection) we found the structure to be extremely difficult to solve. Most of the difficulty was associated with the assignment of *z* coordinates to the heavy atoms and with the determination of the orientations of the sulfate and bisulfate groups.

Neither sharpened nor unsharpened three-dimensional Patterson maps gave clear indications as to the positions of the cobalt or sulfur atoms, but a plausible set of coordinates was eventually assigned to five heavy atoms – all that were thought to be present. Structure factors and a three-dimensional electron-density map were then calculated. This map gave no additional information other than suggesting the orientations of the ligands about the cobalt atoms; in particular, there was no hint of a fourth sulfur atom or of the oxygen atoms of the sulfate or bisulfate groups. Further attempts at three-dimensional refinement were unsuccessful, and we turned our attention to the three centrosymmetric projections.

Difference maps based on the *hk*0 data soon suggested, and chemical analysis confirmed, that there are four sulfur atoms in the formula rather than the three we had originally assumed. The additional atom, S(4), had *x* and *y* coordinates nearly the same as those of S(3); in view of the weakness of the reflections with *l* odd, we assigned it a *z* coordinate $\frac{1}{2}$ greater than that of S(3). The *x* and *y* coordinates of the N and O atoms were assigned and the positions of all 34 non-hydrogen atoms were adjusted by successive structure-factor difference-map calculations until the *R* index for the *hk*0 reflections was 0·12. ($R=\Sigma\ |F_o-F_c|/\Sigma\ F_o$). However, attempts to confirm or improve the *z* coordinates, either by three-dimensional electron-density calculations or by projections down the *a* or *b* axes, were unsuccessful. A trial-and-error search for the *z* coordinates was then initiated.

Eleven different three-dimensional models were tested by three-dimensional structure-factor, least-squares and electron-density calculations and by projections down the *a* and *b* axes. For each of 39 separate structure-factor calculations the *R* index was in the range 0·35–0·40 and the indicated shifts in atomic positions always led to unreasonable structures. Some improvement resulted from incrementing the original *z* coordinates by $\frac{1}{4}$ – a change that affected the calculated intensities of only the weak layer lines with *l* odd – but *R* still remained at about 0·30. The failure of three-dimensional electron-density maps to give back significantly more information than was put into them was a continuing disappointment.

A convergent model was finally obtained by arbitrarily interchanging the *z* coordinates of S(3) and S(4) – a change equivalent to a shift of about 0·5 Å in the positions of these two atoms. After four least-squares cycles and two three-dimensional difference summations, which indicated reasonable positions for the oxygen atoms, the *R* index was 0·28; eight additional least-squares cycles, in which all 102 positional parameters of the heavier atoms were included in one matrix and their 34 isotropic temperature factors in a second, reduced *R* to 0·13 and confirmed the trial structure.

All calculations were carried out on an IBM 7094 computer using subprograms operating under the CRYRM system (Duchamp, 1964). Atomic form factors for Co^{2+} (not corrected for anomalous dispersion), S, O, N, and H were taken from *International Tables for X-ray Crystallography* (1962). The quantity minimized in the least-squares calculations was $\Sigma\ w(F_o^2-F_c^2)^2$. Unobserved reflections were included only if F_c exceeded the threshold value of F_o. Various weighting functions were used, depending upon the stage of the refinement. During the final cycles, the weights *w* were set equal to $1/\sigma^2(F_o^2)$ as calculated during the initial data processing, five very strong reflections which appeared to suffer from extinction (230, 400, 002, 102, and 302) being given zero weight. The 30 ammine hydrogen atoms were introduced at tetrahedral positions 1 Å from the nitrogen atoms; their orientations about the Co–N bonds were chosen by examining difference maps calculated in their planes and by considering the potential hydrogen bonding. The three hydrogen atoms of the bisulfate groups were positioned in a similar manner, and all hydrogen atoms were assigned isotropic temperature factors with $B=2·0$; their positions were not refined, but were readjusted on the basis of a second set of difference maps computed toward the end of the refinement.

During the refinement with isotropic temperature factors, it was apparent that the scaling together of the data for the different layer lines about **c** – which had been based on the rather poor *h*0*l* photographs – was not correct. Accordingly, the layer scale factors were adjusted twice on the basis of F_c, the maximum adjustment being about 30%. These layer scale factors were kept fixed after anisotropic temperature factors were introduced.

Only the six heavy atoms were given anisotropic temperature factors in the next six cycles of least-

Table 2. *Observed structure factors, their estimated standard deviations, the calculated structure factors* (*all* × 10) *and phase angles* (°)

A minus sign indicates an unobserved reflection; asterisks in the e.s.d. column indicate the reflection was given zero weight.

0 K 0				
0	---		14454	0
2	1116	53	1215	0
4	970	40	978	0
6	1023	49	1122	180
8	118	19	127	180
10	440	18	453	180
12	128	19	138	0
14	302	11	297	180
16	-99	36	75	0
1 K 0				
1	-41	***	91	270
2	487	24	492	270
3	776	34	781	90
4	334	11	344	90
5	731	29	763	90
6	194	12	170	270
7	182	14	192	270
8	666	24	709	90
9	503	17	482	270
10	127	22	158	90
11	338	16	330	270
12	512	18	518	270
13	150	14	104	270
14	323	14	324	270
15	299	26	264	90
16	222	21	156	270
17	249	20	221	90
2 K 0				
0	362	19	403	0
1	245	7	275	180
2	464	34	473	0
3	3020	***	4626	180
4	-75	25	87	180
5	127	12	158	180
6	-90	30	83	0
7	413	14	442	180
8	303	14	276	180
9	872	42	885	0
10	140	21	124	180
11	185	18	159	180
12	144	18	132	180
13	166	13	165	0
14	-107	40	18	0
15	-106	38	6	0
16	-98	36	19	0
17	271	21	240	0
3 K 0				
1	549	26	593	90
2	549	29	546	90
3	908	39	920	90
4	-79	26	17	90
5	189	11	191	90
6	434	14	489	270
7	225	13	236	270
8	862	46	875	270
9	818	37	786	270
10	143	21	124	270
11	821	41	876	270
12	439	16	396	90
13	193	12	143	270
14	137	27	106	90
15	317	26	311	90
16	132	19	123	90
17	244	20	203	90
4 K 0				
0	2657	***	4684	180
1	1243	42	1314	180
2	127	14	55	180
3	173	10	140	0
4	264	11	218	0
5	246	12	253	180
6	1525	57	1623	0
7	264	14	275	180
8	554	18	593	0
9	171	18	162	180
10	186	19	205	0
11	399	16	396	0
12	303	14	271	180
13	-113	45	30	0
14	198	24	166	0
15	205	22	175	0
16	-94	34	18	0
17	-69	25	21	0
5 K 0				
1	683	34	780	90
2	129	11	125	270
3	894	40	841	270
4	643	25	623	270
5	462	14	476	270
6	1148	56	1152	270
7	299	14	289	270
8	1129	59	1276	270
9	498	18	449	90
10	200	18	196	270
11	265	15	259	90
12	578	31	535	90
13	-111	44	68	90
14	336	28	282	90
15	147	21	102	270
16	218	35	141	90
17	63	23	53	270
6 K 0				
0	126	17	94	0
1	518	19	590	0
2	362	12	408	180
3	937	43	1083	0
4	429	13	427	0
5	474	15	489	0
6	74	43	94	0
7	292	15	321	180
8	1059	57	1093	0
9	1083	61	1047	180
10	244	17	262	0
11	-118	47	59	180
12	294	13	308	0
13	-109	41	28	0
14	71	33	91	180
15	87	23	68	0
16	-84	31	16	0
17	132	21	106	180
7 K 0				
1	264	11	285	270
2	145	18	64	270
3	514	15	540	270
4	814	44	897	270
5	195	14	184	270
6	317	16	310	90
7	340	16	362	90
8	563	20	560	90
9	1254	63	1235	90
10	214	16	202	90
11	785	47	873	90
12	137	12	133	270
13	183	34	192	90
14	-106	38	2	90
15	194	20	166	270
16	-76	28	10	270
8 K 0				
0	891	43	1010	0
1	639	24	668	0
2	354	13	382	0
3	240	13	236	0
4	727	36	743	180
5	565	18	609	0
6	915	41	919	180
7	-112	38	65	0
8	321	17	331	180
9	332	16	345	0
10	243	15	259	0
11	476	20	431	180
12	222	10	222	0
13	-108	39	6	0
14	-103	37	37	180
15	252	21	185	180
16	123	24	80	180
9 K 0				
1	1026	52	1149	270
2	161	15	170	270
3	448	15	446	90
4	537	17	549	90
5	360	16	374	90
6	850	43	828	90
7	461	18	506	90
8	716	33	714	90
9	-118	46	72	90
10	231	14	239	90
11	-113	45	45	90
12	357	29	347	270
13	-106	38	25	270
14	220	36	130	270
15	-82	30	90	90
16	204	28	165	270
10 K 0				
0	657	25	651	0
1	515	17	534	180
2	766	32	820	0
3	737	33	814	180
4	-110	37	61	180
5	199	17	186	180
6	-115	40	17	180
7	462	18	456	0
8	719	36	664	180
9	408	15	399	0
10	-114	47	57	180
11	-109	42	24	0
12	267	25	275	180
13	155	34	100	180
14	76	37	95	0
15	-72	26	75	180
11 K 0				
1	-111	37	67	90
2	814	38	885	90
3	206	17	235	90
4	663	26	704	90
5	267	17	247	90
6	147	20	94	90
7	158	18	137	90
8	-117	48	41	270
9	461	20	444	270
10	-111	43	63	270
11	268	25	249	270
12	-106	38	65	90
13	-99	36	87	270
14	-82	30	81	270
15	188	27	170	90
12 K 0				
0	925	44	962	180
1	561	21	593	180
2	156	20	146	180
3	350	17	379	180
4	245	16	253	0
5	529	18	551	180
6	328	15	332	0
7	197	15	162	180
8	-115	47	71	0
9	124	12	147	180
10	262	26	278	180
11	261	24	213	0
12	-101	37	98	180
13	-90	33	9	180
14	-69	25	18	0
13 K 0				
1	1024	57	1024	90
2	323	16	313	90
3	213	16	215	90
4	173	17	192	90
5	209	15	216	270
6	147	16	152	270
7	173	13	168	270
8	113	31	121	270
9	-108	40	5	270
10	-107	39	109	270
11	89	40	103	270
12	230	37	150	90
13	-76	28	64	90
14	109	18	99	90
14 K 0				
0	447	17	446	180
1	155	18	116	0
2	700	42	755	180
3	403	15	392	0
4	177	15	143	180
5	-115	47	48	180
6	-113	46	54	0
7	294	13	294	180
8	255	26	264	0
9	200	23	183	180
10	155	34	130	0
11	-96	35	11	0
12	123	28	110	0
13	302	888	214	0
15 K 0				
1	284	14	280	90
2	417	16	429	270
3	-114	47	23	270
4	304	14	348	270
5	78	16	62	270
6	136	8	120	270
7	205	35	174	270
8	-106	38	51	90
9	108	36	104	90
10	147	33	126	90
11	183	31	133	90
16 K 0				
0	162	11	168	0
1	241	11	240	0
2	-109	33	58	180
3	138	9	123	0
4	141	7	151	180
5	178	34	175	0
6	220	35	204	180
7	-105	38	154	0
8	135	34	86	0
9	-94	35	9	180
10	432	38	368	0
11	115	22	89	180
17 K 0				
1	301	33	319	270
2	161	35	161	270
3	100	40	94	270
4	137	35	145	270
5	147	34	112	90
6	88	40	54	90
7	424	37	317	90
8	163	31	149	90
9	133	27	94	90
10	199	28	102	90
18 K 0				
0	93	40	56	0
1	65	50	75	180
2	-104	37	105	0
4	-100	36	11	180
5	-97	36	90	0
6	-91	34	68	180
7	400	39	300	0
9	157	23	141	0
19 K 0				
1	136	33	139	270
2	122	33	141	90
4	323	45	228	90
5	184	30	140	90
6	123	25	86	90
7	194	28	136	90
20 K 0				
4	164	26	105	0
0 K 1				
1	-18	***	4	90
2	318	13	391	0
3	-31	9	35	90
4	200	7	193	180
5	588	22	554	270
6	806	37	784	180
7	532	18	512	90
8	376	14	386	180
9	135	11	129	90
10	237	13	205	180
11	107	12	108	270
12	53	16	38	180
13	155	8	147	90
14	-30	9	27	0
1 K 1				
0	119	20	123	90
1	-20	***	617	14
2	473	17	523	197
3	263	8	266	332
4	205	9	182	70
5	648	27	640	75
6	360	12	362	117
7	223	9	225	150
8	373	14	392	93
9	253	17	295	166
10	57	20	65	96
11	240	16	218	47
12	169	9	153	22
13	100	9	61	70
14	169	9	158	132
2 K 1				
0	-56	16	13	90
1	346	13	356	328
2	58	6	42	285
3	390	14	428	83
4	147	7	139	204
5	711	34	755	187
6	306	12	312	28
7	454	14	460	133
8	325	14	275	92
9	136	12	92	259
10	180	12	163	266
11	253	13	218	107
12	201	9	203	261
13	188	9	166	322
14	81	6	75	63
3 K 1				
0	243	7	252	270
1	256	8	292	145
2	304	9	349	176
3	259	9	262	236
4	269	10	269	263
5	487	17	430	160
6	543	18	534	166
7	453	14	444	55
8	397	15	418	308
9	128	12	117	354
10	80	16	53	300
11	283	15	292	146
12	238	10	245	357
13	74	10	76	36
4 K 1				
0	509	21	483	90
1	212	8	223	87
2	587	23	542	318
3	700	31	738	357
4	572	23	577	98
5	275	11	277	72
6	323	12	330	226
7	387	14	414	258
8	274	16	281	14
9	351	17	370	223
10	343	17	343	303
11	51	18	39	58
12	276	11	272	83
13	62	10	59	321
5 K 1				
0	203	9	180	270
1	453	14	487	272
2	269	10	250	187
3	236	10	213	61
4	260	11	240	112
5	379	12	406	28
6	185	9	162	132
7	252	10	241	14
8	338	16	374	207
9	539	20	568	344
10	209	11	197	327
11	85	13	85	222
12	190	9	202	155
13	82	8	40	102
6 K 1				
0	203	10	201	270
1	430	15	444	174
2	459	14	463	40
3	1131	37	1319	194
4	170	8	148	176
5	268	13	222	34
6	335	14	343	204
7	556	19	557	286
8	127	13	115	273
9	268	18	272	69
10	363	15	361	90
11	99	12	68	290
12	238	10	226	59
13	153	6	153	98
7 K 1				
0	223	11	226	90
1	165	8	148	186
2	337	12	360	46
3	497	16	529	118
4	399	13	391	77
5	244	14	213	52
6	287	15	296	340
7	153	12	116	284
8	291	14	259	224
9	247	12	215	170
10	114	11	103	131
11	386	12	383	3
12	130	7	124	147
8 K 1				
0	236	12	235	270
1	583	19	628	232
2	230	13	227	0
3	526	16	531	163
4	305	14	297	299
5	396	15	405	242
6	367	16	338	55
7	261	18	311	74
8	295	17	321	114
9	250	13	260	68
10	309	12	271	90
11	159	8	153	73
12	73	7	92	241
9 K 1				
0	75	12	58	270
1	443	15	484	350
2	108	11	60	338
3	123	11	107	299
4	125	11	111	58
5	57	19	73	217
6	173	11	182	213
7	79	15	103	161
8	320	15	336	28
9	142	10	141	102
10	188	11	193	181
11	113	7	112	117
10 K 1				
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1	347	15	355	25
2	549	18	509	255
3	201	11	207	63
4	429	17	442	66
5	138	13	107	155
6	237	12	191	207
7	157	10	171	58
8	426	14	420	107
9	89	12	46	226
10	136	7	148	299
11	132	7	124	268
11 K 1				
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1	234	18	213	26
2	225	12	217	218
3	137	12	149	337
4	320	18	292	137
5	95	13	91	74
6	119	11	129	72
7	-54	17	36	256
8	121	10	119	132
9	157	8	149	20
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12 K 1				
0	323	17	333	90
1	601	25	625	84
2	205	11	213	128
3	181	11	136	268
4	67	15	82	48
5	498	16	515	100
6	149	10	140	58
7	259	11	204	249
8	184	8	197	265
9	43	10	22	338
13 K 1				
0	38	23	11	90
1	376	15	372	148
2	74	13	69	121
3	179	10	173	76
4	109	11	109	213
5	175	10	141	222
6	93	10	70	339
7	106	8	81	338
8	108	6	90	193
14 K 1				
0	82	12	62	90
1	94	12	61	246
2	479	15	473	84
3	64	14	43	24
4	324	11	318	275
5	154	8	146	252
6	161	8	153	58
7	58	8	71	126
15 K 1				
0	160	8	132	90
1	77	11	71	216
2	55	13	42	56
3	45	14	45	194
4	86	8	73	347
5	70	7	69	334
6	191	9	136	248
16 K 1				
0	32	12	39	90
1	313	11	324	271
2	73	6	77	284
3	75	5	80	79
0 K 2				
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1	-30	***	306	270
2	624	13	648	180
3	723	60	765	270
4	1424	119	1640	0
5	370	19	393	270
6	840	48	832	180
7	169	15	136	270
8	112	24	109	0
9	728	36	708	90
10	255	19	252	180
11	850	59	919	90
12	399	21	349	0
13	339	17	274	90
1 K 2				
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2	1412	88	1356	356
3	1705	106	1777	6
4	199	10	210	247
5	763	44	801	57
6	1032	51	1056	168
7	119	19	81	342
8	485	21	469	131
9	448	30	439	237
10	338	19	311	269
11	138	20	143	203
12	397	21	369	258
13	-72	22	14	93
2 K 2				
0	135	6	136	180
1	1098	84	1046	334
2	1039	101	982	311
3	1989	114	1982	180
4	330	12	312	43
5	596	29	551	166
6	946	51	923	92
7	668	29	644	159
8	709	32	745	101
9	665	34	651	13
10	372	19	375	89
11	314	17	287	131
12	438	21	415	257
13	226	12	199	18
3 K 2				
0	1962	***	2395	0
1	894	50	808	175
2	1590	108	1697	357
3	1117	131	1093	157
4	270	11	273	218
5	581	24	546	128
6	705	33	695	195
7	78	31	90	57
8	716	33	722	208
9	558	32	487	305
10	206	19	165	181
11	144	19	168	11
12	309	18	288	96
13	171	11	157	198
4 K 2				
0	1461	85	1706	180
1	564	35	493	178
2	1000	46	910	7
3	547	27	543	125
4	946	47	876	44
5	1032	51	1031	129
6	1002	54	1001	8
7	246	15	196	100
8	275	17	213	130
9	775	47	820	253
10	260	17	248	357
11	801	51	761	287
12	335	19	309	231
13	144	11	137	271
5 K 2				
0	237	10	233	0
1	892	43	968	153
2	894	44	886	218
3	1137	54	1286	226
4	340	13	319	327
5	1081	54	1117	175
6	850	55	827	313
7	65	38	27	356
8	258	18	221	324
9	468	25	411	41
10	332	17	336	175
11	205	17	197	35
12	266	14	216	125
13	123	9	127	67
6 K 2				
0	352	17	382	0
1	1037	49	1000	27
2	795	46	723	120
3	1126	53	1214	33
4	361	14	355	3
5	125	18	67	271
6	779	38	811	269
7	534	30	562	277
8	919	71	903	303
9	533	31	573	229
10	318	16	324	248
11	393	18	383	286
12	412	17	393	54
13	106	10	118	214
7 K 2				
0	906	46	909	180
1	599	25	578	334
2	1009	51	1066	186
3	182	14	167	262
4	608	26	603	321
5	240	15	225	49
6	700	34	692	28
7	533	32	499	190
8	596	33	572	5
9	474	22	434	125
10	160	18	189	48
11	123	16	96	95
12	98	14	82	250
8 K 2				
0	671	31	608	0
1	595	24	571	48
2	413	16	382	280
3	268	14	234	266
4	780	39	812	230
5	800	42	824	311
6	775	45	726	238
7	333	19	324	235
8	393	29	400	264
9	539	26	563	50
10	-89	27	23	140
11	620	37	544	125
12	243	11	237	65
9 K 2				
0	403	23	416	180
1	785	38	819	326
2	349	16	327	29
3	895	62	925	33
4	414	18	390	155
5	601	33	626	351
6	376	19	341	111
7	358	19	346	102
8	237	17	217	16
9	295	15	298	188
10	424	19	382	15
11	133	11	105	135
10 K 2				
0	328	17	301	180
1	557	30	536	231
2	707	35	686	307
3	664	34	641	233
4	458	21	465	256
5	332	19	291	165
6	418	19	430	43
7	338	18	318	89
8	550	25	538	131
9	409	17	393	70
10	209	12	194	43
11	273	12	279	104
11 K 2				
0	832	66	854	0
1	287	19	253	139
2	539	33	506	18
3	231	19	219	37
4	530	32	477	125
5	423	19	355	14
6	549	27	518	158
7	502	24	457	37
8	254	14	204	161
9	315	15	265	329
10	146	9	149	258
12 K 2				
0	438	20	389	180
1	736	46	693	244
2	366	18	330	120
3	125	23	135	26
4	384	18	332	85
5	565	27	530	128
6	438	22	378	64
7	232	15	204	97
8	272	13	214	63
9	191	9	197	207
13 K 2				
0	319	16	288	0
1	450	21	354	125
2	232	17	180	16
3	542	25	535	170
4	268	15	239	30
5	239	15	234	156
6	80	21	110	347
7	191	12	168	309
8	309	13	291	172
14 K 2				
0	112	19	149	0
1	271	15	234	67
2	570	25	544	126
3	291	15	266	65
4	524	22	459	89
5	-74	22	37	315
6	37	30	60	187
7	172	9	160	227
15 K 2				
0	512	23	449	180
1	-77	23	46	136
2	298	13	268	234
3	55	24	75	235
4	169	11	165	324
5	292	13	258	176
16 K 2				
0	-55	17	46	0
1	425	27	479	77
2	70	12	56	215
3	130	7	136	81
0 K 3				
1	237	10	248	270
2	-53	15	57	0
3	310	11	272	270
4	1196	43	1197	0
5	861	42	845	270
6	285	14	244	0
7	187	17	175	270
8	120	28	115	180
9	-109	39	26	270
10	478	21	450	180
11	280	17	277	270
12	57	46	17	180
13	-73	22	85	270
1 K 3				
0	-81	23	27	270
1	567	22	468	338
2	556	27	444	173
3	869	34	745	2
4	430	19	373	311
5	678	44	570	39
6	780	47	812	189
7	344	16	345	13
8	245	19	254	111
9	367	20	368	121
10	356	19	357	128
11	136	23	154	341
12	100	21	141	53
13	234	11	224	234
2 K 3				
0	82	8	64	270
1	152	8	135	60
2	461	30	380	35
3	140	11	112	206
4	219	12	186	205
5	744	43	696	186
6	378	15	399	67
7	642	29	642	169
8	593	25	551	102
9	86	41	113	280
10	84	39	87	276
11	-110	34	89	139
12	56	45	33	196
13	186	10	180	333
3 K 3				
0	217	9	205	270
1	269	10	245	69
2	892	34	838	179
3	422	19	371	137
4	518	22	500	28
5	473	22	456	121
6	654	34	651	127
7	478	18	458	118
8	208	21	202	290
9	170	24	195	0
10	144	25	164	159
11	194	18	212	182
12	100	22	84	306
13	237	10	236	304
4 K 3				
0	126	11	98	270
1	309	11	322	179
2	1148	42	1124	183
3	216	12	213	321
4	723	44	715	185
5	473	16	439	187
6	362	16	317	208
7	-107	34	19	113
8	191	22	175	83
9	105	33	113	253
10	317	18	361	317
11	63	50	65	50
12	84	20	106	91
5 K 3				
0	56	30	12	90
1	495	21	514	18
2	515	22	527	82
3	1218	46	1247	35
4	522	23	530	149
5	490	17	461	0
6	202	18	168	353
7	281	19	255	135
8	171	24	185	142
9	125	29	129	328
10	195	19	158	346
11	-104	32	45	156
12	137	13	149	203
6 K 3				
0	120	16	130	90
1	940	43	985	194
2	523	22	554	226
3	638	31	614	223
4	317	15	305	171
5	577	27	551	16
6	207	19	212	159
7	226	21	203	282
8	-108	38	99	307
9	-110	36	36	185
10	248	17	239	101
11	117	18	131	281
12	157	11	137	46
7 K 3				
0	817	45	772	90
1	374	15	373	195
2	380	15	347	18
3	-100	29	83	65
4	466	17	409	197
5	179	20	200	281
6	241	20	225	265
7	159	25	172	48
8	178	22	141	125
9	164	21	132	147
10	-107	33	17	272
11	204	13	194	17
12	34	27	43	33
8 K 3				
0	73	36	37	90
1	459	17	479	199
2	568	22	573	17
3	248	17	245	128
4	251	18	253	351
5	226	20	198	154
6	291	20	269	66
7	285	19	247	62
8	102	38	98	212
9	176	19	154	5
10	246	14	277	117
11	-75	23	81	123
9 K 3				
0	-106	33	37	270
1	251	18	235	192
2	222	19	200	327
3	491	21	507	223
4	135	27	146	15
5	77	52	113	245
6	132	32	159	248
7	91	56	55	102
8	210	18	218	25
9	166	17	127	117
10	131	14	116	191
11	96	9	112	41
10 K 3				
0	244	19	208	90
1	225	20	171	280
2	242	20	222	280
3	196	23	147	112
4	365	20	407	35
5	263	19	282	159
6	197	21	220	328
7	279	17	296	135
8	247	16	242	70
9	52	42	71	65
10	184	10	199	259
11 K 3				
0	-109	39	33	90
1	190	22	214	352
2	178	24	185	261
3	-107	37	74	208
4	74	50	96	166
5	222	19	206	60
6	338	17	364	119
7	61	50	67	7
8	75	32	70	143
9	99	13	104	82
12 K 3				
0	147	25	110	270
1	370	19	357	93
2	-110	36	63	97
3	230	19	220	263
4	345	17	337	126
5	441	20	473	85
6	219	15	205	53
7	183	14	188	218
8	121	12	112	347
13 K 3				
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1	220	18	228	159
2	66	50	83	178
3	198	17	204	108
4	60	49	80	162
5	172	15	157	112
6	110	22	91	83
14 K 3				
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2	385	15	356	91
3	170	14	165	74
4	205	13	201	243
5	116	12	112	316
6	209	9	234	119
15 K 3				
0	140	12	132	90
1	61	20	117	186
2	132	12	123	55
3	56	24	42	96
4	83	10	99	356
0 K 4				
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2	1249	58	1303	180
3	127	13	132	90
4	727	47	726	0
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6	417	18	368	0
7	353	19	341	90
8	906	52	866	0
9	549	36	596	90
10	198	25	188	180
11	667	28	675	90
12	170	16	147	0
13	178	9	172	90
1 K 4				
0	897	123	959	180
1	499	26	422	176
2	150	10	136	62
3	918	41	831	337
4	104	21	138	356
5	887	53	902	332
6	944	59	974	215
7	156	25	162	294
8	609	29	641	233
9	362	22	352	120
10	139	30	150	339
11	491	20	522	118
12	310	15	270	89
13	145	9	156	82
2 K 4				
0	363	15	364	180
1	938	37	795	1
2	699	37	598	232
3	767	43	718	348
4	476	24	430	110
5	1230	55	1285	350
6	750	35	683	75
7	475	21	467	159
8	675	39	648	97
9	250	23	246	72
10	166	27	158	325
11	301	18	315	195
12	208	14	196	279
13	125	8	147	355
3 K 4				
0	518	29	584	0
1	548	24	457	196
2	791	41	732	331
3	640	32	586	228
4	294	15	267	319
5	509	22	496	249
6	769	36	744	150
7	260	21	232	46
8	501	24	468	130
9	343	22	317	91
10	205	23	165	99
11	671	36	643	67
12	118	16	108	255
4 K 4				
0	598	26	649	0
1	210	13	198	59
2	1225	50	1232	6
3	589	26	514	356
4	647	28	616	165
5	821	41	731	77
6	386	19	335	128
7	314	21	295	10
8	546	25	545	179
9	288	23	263	237
10	267	21	288	322
11	333	17	361	290
12	155	13	145	244
5 K 4				
0	282	13	229	0
1	453	23	521	230
2	334	15	293	218
3	1222	54	1229	180
4	665	31	628	30
5	1040	63	1108	152
6	449	21	450	68
7	154	29	157	99
8	596	30	552	66
9	95	45	126	117
10	190	21	205	208
11	205	16	199	279
12	199	11	191	264
6 K 4				
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2	594	28	539	57
3	832	60	814	154
4	330	18	296	358
5	743	36	697	167
6	547	25	526	209
7	347	22	342	335
8	181	27	158	318
9	93	43	81	221
10	305	17	340	207
11	164	15	157	355
12	78	10	87	78
7 K 4				
0	887	56	965	180
1	625	30	592	15
2	904	62	1041	148
3	392	19	347	79
4	369	20	371	66
5	603	29	547	85
6	315	22	353	26
7	249	24	272	218
8	260	22	273	299
9	111	30	147	310
10	-97	29	56	13
11	415	18	443	267
8 K 4				
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1	239	20	203	84
2	653	35	554	225
3	897	49	838	183
4	499	23	466	320
5	461	23	436	247
6	380	22	350	311
7	521	24	551	207
8	311	20	279	314
9	216	18	237	6
10	217	14	237	153
11	176	9	180	116
9 K 4				
0	129	40	125	180
1	470	22	470	52
2	331	21	316	46
3	729	41	660	27
4	347	22	315	228
5	722	39	701	325
6	334	22	292	271
7	121	38	125	308
8	447	19	437	271
9	167	16	213	238
10	204	12	200	358
10 K 4				
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1	236	23	197	301
2	294	22	255	292
3	634	30	522	315
4	380	22	405	241
5	215	24	173	315
6	472	21	507	358
7	403	19	420	135
8	226	16	216	73
9	219	13	217	144
11 K 4				
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1	156	29	155	159
2	392	22	403	304
3	217	25	139	296
4	436	21	429	255
5	457	21	420	290
6	407	18	416	229
7	225	16	208	16
8	188	13	173	127
9	201	9	207	69
12 K 4				
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1	193	24	151	250
2	117	32	90	96
3	501	22	544	0
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5	364	17	383	67
6	484	20	442	127
7	364	14	369	31
8	141	13	163	66
13 K 4				
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1	274	18	274	267
2	248	18	200	270
3	321	16	319	220
4	-94	28	58	339
5	275	14	256	112
6	167	12	162	82
7	185	8	204	70
14 K 4				
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2	273	14	254	82
3	272	13	263	135
4	270	12	253	70
5	119	10	123	14
15 K 4				
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2	230	10	236	82
0 K 5				
1	292	12	253	270
2	432	17	441	0
3	106	9	115	270
4	828	40	737	0
5	250	12	229	270
6	205	13	184	180
7	450	31	441	270
8	113	20	71	180
9	193	17	215	270
10	183	14	197	180
11	56	17	60	90
12	33	14	51	0
1 K 5				
0	132	55	67	270
1	446	22	449	296
2	178	8	188	1
3	434	19	432	22
4	719	37	727	335
5	409	25	369	32
6	245	13	240	48
7	471	30	454	11
8	278	18	277	74
9	193	17	201	82
10	361	21	340	147
11	56	17	30	280
12	161	9	157	77
2 K 5				
0	189	9	178	90
1	748	57	787	1
2	276	17	246	316
3	327	19	329	251
4	416	22	374	240
5	555	27	497	222
6	131	14	102	302
7	355	22	343	189
8	65	29	103	276
9	138	17	137	297
10	193	13	201	99
11	123	11	129	137
12	108	8	114	83
3 K 5				
0	106	8	110	90
1	675	32	649	5
2	432	19	459	357
3	148	10	164	12
4	693	41	749	26
5	269	13	268	87
6	293	15	256	104
7	296	18	266	139
8	241	18	214	261
9	60	27	69	104
10	156	13	143	145
11	89	12	84	198
12	75	7	69	242
4 K 5				
0	410	18	424	270
1	72	12	53	232
2	539	23	486	202
3	214	11	219	320
4	647	29	580	160
5	129	14	111	139
6	-66	23	43	218
7	80	24	66	226
8	209	18	146	83
9	41	35	47	219
10	155	12	161	355
11	63	12	49	222
5 K 5				
0	168	10	174	270
1	590	39	707	359
2	583	25	532	123
3	466	25	389	122
4	484	27	457	171
5	198	14	183	216
6	-69	25	17	112
7	65	29	66	104
8	170	17	158	212
9	154	14	161	297
10	185	12	190	310
11	115	9	130	59
6 K 5				
0	296	13	279	270
1	693	34	596	156
2	267	13	244	125
3	486	27	445	132
4	241	14	215	102
5	339	18	320	55
6	134	18	141	139
7	331	19	325	309
8	-72	23	54	140
9	186	13	215	130
10	90	12	116	88
11	111	7	107	281
7 K 5				
0	498	25	466	90
1	318	15	310	198
2	534	29	505	187
3	179	14	153	62
4	337	18	325	179
5	308	18	295	282
6	274	18	265	253
7	43	38	74	323
8	210	14	222	88
9	83	14	85	264
10	105	10	98	313
8 K 5				
0	65	23	73	90
1	245	15	210	218
2	442	32	355	62
3	413	31	410	112
4	449	31	380	327
5	162	18	138	235
6	106	20	112	150
7	194	14	200	27
8	51	22	71	127
9	105	11	108	16
10	174	9	189	137
9 K 5				
0	46	37	52	270
1	165	17	172	144
2	145	18	107	212
3	364	30	357	259
4	100	22	89	351
5	155	17	152	25
6	198	14	204	198
7	159	13	130	340
8	215	11	224	121
9	131	9	108	20
10 K 5				
0	372	25	340	90
1	155	18	111	355
2	243	17	202	280
3	139	18	145	169
4	244	15	235	31
5	243	14	251	241
6	262	14	254	299
7	247	12	248	138
8	141	9	122	90
9	65	6	75	2
11 K 5				
0	161	16	128	270
1	164	16	160	239
2	101	19	93	330
3	128	15	87	145
4	121	14	96	24
5	263	13	260	136
6	306	17	275	54
7	103	9	85	117
8	86	6	99	262
12 K 5				
0	165	13	149	90
1	328	17	349	83
2	82	17	41	209
3	306	16	298	277
4	154	11	152	173
5	138	10	115	118
6	229	13	216	20
7	171	9	168	183
13 K 5				
0	108	11	103	90
1	137	11	160	161
2	74	12	80	285
3	187	10	164	104
4	88	9	96	130
5	124	7	129	170
14 K 5				
0	172	9	180	270
1	91	8	77	238
2	164	8	156	113
3	145	9	141	57
0 K 6				
0	-119	37	57	180
1	139	7	140	270
2	1035	41	910	180
3	714	29	602	90
4	831	33	738	0
5	497	22	467	90
6	425	22	399	0
7	358	18	337	90
8	689	29	701	0
9	599	25	601	270
10	58	14	39	180
11	64	9	33	270
1 K 6				
0	644	84	641	180
1	262	10	270	171
2	309	14	236	167
3	768	32	596	198
4	100	12	95	208
5	770	35	690	204
6	701	35	689	294
7	252	15	240	145
8	421	18	424	266
9	337	15	379	54
10	-50	15	40	35
11	341	21	362	96
2 K 6				
0	392	18	362	180
1	683	30	592	7
2	409	17	329	175
3	614	28	540	2
4	495	22	438	143
5	1025	50	1074	9
6	548	24	524	290
7	400	20	376	180
8	266	13	264	262
9	67	15	84	170
10	175	9	176	35
11	226	9	232	173
3 K 6				
0	714	27	695	180
1	108	8	100	305
2	619	28	484	191
3	817	33	703	315
4	214	13	185	316
5	370	22	271	257
6	467	22	410	31
7	159	14	146	76
8	388	17	382	72
9	424	15	479	130
10	123	9	125	82
11	327	13	400	73
4 K 6				
0	492	21	447	0
1	155	10	142	92
2	1027	45	1010	353
3	740	33	612	320
4	581	27	570	180
5	296	17	281	304
6	389	21	357	185
7	358	19	384	7
8	406	16	418	189
9	386	14	419	106
10	153	8	162	71
11	166	7	191	80
5 K 6				
0	639	29	647	0
1	680	32	645	323
2	560	26	471	170
3	727	34	722	1
4	405	22	347	181
5	328	17	325	37
6	581	25	603	124
7	121	14	116	91
8	380	15	399	60
9	95	10	94	153
10	-39	12	28	306
6 K 6				
0	735	32	721	0
1	708	34	660	200
2	430	22	398	349
3	661	35	625	163
4	462	22	488	28
5	665	33	681	169
6	513	20	474	137
7	158	12	178	12
8	322	14	332	91
9	107	9	115	73
10	240	9	246	175
7 K 6				
0	452	21	427	0
1	191	16	188	96
2	311	19	267	108
3	448	22	473	146
4	578	26	620	129
5	429	19	390	49
6	400	17	384	174
7	94	12	96	11
8	220	10	220	234
9	270	10	279	314
8 K 6				
0	508	21	522	180
1	98	21	82	324
2	602	26	642	152
3	657	31	616	159
4	355	18	342	41
5	371	17	378	137
6	346	15	346	49
7	321	14	290	176
8	153	8	155	30
9	142	7	144	307
9 K 6				
0	471	19	482	180
1	493	20	500	115
2	108	17	102	45
3	459	18	456	176
4	139	12	125	313
5	291	15	292	234
6	347	14	350	304
7	229	10	228	253
8	286	10	299	248
10 K 6				
0	474	18	451	180
1	297	15	310	54
2	236	12	253	127
3	379	16	370	24
4	203	10	197	145
5	144	9	155	13
6	334	12	335	4
7	161	7	175	167
11 K 6				
0	396	15	360	180
1	64	15	69	279
2	406	15	362	244
3	158	10	181	326
4	397	16	430	265
5	288	11	290	260
6	238	9	244	302
12 K 6				
0	258	12	266	0
1	179	9	180	82
2	52	12	61	317
3	334	12	329	4
4	185	9	180	217
5	137	7	156	341
13 K 6				
0	79	7	74	0
1	299	12	321	290
2	152	8	154	244
3	195	7	230	336
0 K 7				
1	177	26	111	90
2	261	34	258	180
3	133	39	106	270
4	-82	30	5	180
5	125	44	155	270
6	388	55	372	180
7	440	49	465	270
8	119	31	151	180
9	-58	18	68	270
10	-42	13	19	0
1 K 7				
0	148	22	130	90
1	723	90	505	168
2	545	60	406	352
3	44	88	41	63
4	326	43	288	358
5	383	49	358	35
6	239	35	232	122
7	246	31	290	25
8	230	27	261	105
9	58	35	101	340
10	103	16	141	163
2 K 7				
0	49	52	71	270
1	231	31	139	190
2	58	62	102	228
3	64	68	47	168
4	388	49	320	266
5	343	42	310	212
6	156	36	168	54
7	89	44	51	103
8	118	29	107	96
9	142	22	146	327
10	241	24	288	83
3 K 7				
0	82	49	100	270
1	501	58	385	27
2	314	41	204	19
3	273	40	243	295
4	453	60	407	4
5	251	37	252	151
6	-81	26	89	308
7	171	30	197	175
8	214	26	242	264
9	122	21	135	291
10	118	13	127	164
4 K 7				
0	-78	29	58	90
1	131	42	83	37
2	373	49	258	309
3	525	62	509	338
4	222	38	162	163
5	176	36	165	41
6	79	49	70	326
7	259	29	291	82
8	214	25	224	83
9	124	19	133	94
5 K 7				
0	259	33	217	270
1	691	72	597	333
2	204	40	219	112
3	343	42	319	3
4	258	36	259	175
5	163	34	184	267
6	121	35	114	68
7	265	28	250	185
8	140	23	161	319
9	136	17	166	200
6 K 7				
0	275	32	230	270
1	235	38	159	155
2	227	38	199	51
3	308	38	241	203
4	-81	26	18	118
5	299	32	286	83
6	277	29	282	116
7	-63	19	63	138
8	135	20	137	264
9	88	12	99	126
7 K 7				
0	162	32	166	90
1	202	36	197	230
2	200	35	156	224
3	224	33	234	87
4	379	41	363	150
5	141	30	154	296
6	132	26	157	190
7	79	28	84	34
8	145	17	164	59
8 K 7				
0	46	77	18	90
1	200	33	218	287
2	281	32	247	79
3	377	37	437	119
4	151	28	165	6
5	132	26	125	251
6	-57	17	41	131
7	89	21	114	282
9 K 7				
0	-73	22	45	270
1	358	36	370	149
2	100	36	109	295
3	186	26	177	205
4	51	44	67	53
5	198	22	222	35
6	127	18	138	216
7	95	12	136	337
10 K 7				
0	428	34	449	90
1	185	25	191	323
2	162	24	156	245
3	67	32	76	294
4	-52	16	17	49
5	141	17	143	273
6	129	12	171	254
11 K 7				
0	56	28	74	270
1	43	36	62	94
2	223	22	257	33
3	113	17	122	158
4	93	14	102	13
12 K 7				
0	166	14	175	270
1	92	13	152	159
2	59	11	76	264
0 K 8				
0	-116	39	2	180
1 K 8				
0	998	169	1124	180
2 K 8				
0	-116	38	42	0
3 K 8				
0	1065	161	1180	180
4 K 8				
0	267	53	217	180
5 K 8				
0	425	58	449	0
6 K 8				
0	122	67	90	0
7 K 8				
0	580	120	604	0
8 K 8				
0	225	50	213	0
9 K 8				
0	323	50	350	180
10 K 8				
0	191	33	122	180
1 K 9				
0	198	54	172	90
2 K 9				
0	183	54	199	270
3 K 9				
0	108	66	145	270
4 K 9				
0	59	96	15	90
0 K 10				
0	870	90	878	0
1 K 10				
0	301	75	343	180
2 K 10				
0	141	31	111	0
3 K 10				
0	208	31	240	180

squares refinement; the R index fell to 0·091, and the goodness of fit to 1·9. Six more cycles completed the refinement. A total of 307 parameters were adjusted: three coordinates and six temperature factors for the 34 heavier atoms, and a scale factor. Because of the limited core storage available in the computer, all 307 could not be included in a single matrix. For the last cycles, the 102 coordinates were included in one matrix and the temperature parameters in six additional matrices, one for each heavy atom and its ligands. During the last two cycles, the temperature parameters of the six heavy atoms and the scale factor were included in one matrix and the other temperature parameters were not refined. The final shift in any parameter was less than 0·4 times its standard deviation.

The final R index for 1357 observed reflections is 0·078 and the goodness of fit, $[\Sigma\, w(F_o^2-F_c^2)^2/(n-p)]^{\frac{1}{2}}$,

Table 3. *Positional and thermal parameters of the non-hydrogen atoms and their standard deviations*

All values have been multiplied by 10^4. The temperature factors are of the form $\exp\{-(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})\}$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(1)	-1241(1)	-894(1)	10917(3)	33(1)	52(1)	91(3)	-5(1)	2(3)	-7(3)
Co(2)	1008(1)	543(1)	9108(3)	34(1)	52(1)	90(3)	-6(2)	5(2)	2(3)
S(1)	1025(2)	507(2)	3922(4)	36(1)	43(2)	59(5)	3(3)	4(4)	6(5)
S(2)	-1219(2)	-959(2)	6104(4)	33(1)	43(2)	61(5)	3(2)	14(4)	-9(5)
S(3)	3402(2)	2454(2)	10035(6)	36(1)	39(1)	122(6)	-2(3)	2(5)	-4(5)
S(4)	3669(2)	2627(2)	5194(5)	35(1)	46(2)	100(6)	16(3)	-3(5)	-20(6)
N(1)	-1985(7)	-261(8)	9747(14)	45(5)	46(7)	84(24)	1(10)	-7(19)	34(22)
N(2)	-1282(6)	-2028(7)	9761(13)	29(4)	47(6)	72(21)	3(9)	-23(16)	-33(18)
N(3)	-1170(7)	237(7)	12029(15)	39(6)	35(6)	112(21)	-10(10)	43(18)	-11(19)
N(4)	-2151(7)	-1364(9)	12029(14)	41(6)	49(8)	84(22)	-4(11)	10(17)	-7(21)
N(5)	-469(6)	-1571(8)	12098(13)	31(5)	51(7)	57(21)	7(10)	27(16)	8(19)
N(6)	1016(8)	1621(8)	10323(14)	55(6)	52(7)	57(22)	-26(11)	13(18)	-26(19)
N(7)	1846(6)	-44(8)	10239(13)	29(5)	57(7)	41(19)	9(9)	-5(14)	-4(19)
N(8)	171(7)	1178(8)	8040(13)	43(6)	49(7)	88(24)	-6(12)	4(18)	12(21)
N(9)	1857(7)	1110(8)	7954(12)	35(5)	47(7)	36(19)	-6(10)	8(15)	24(18)
N(10)	1018(7)	-586(7)	7953(14)	41(5)	29(6)	82(19)	-6(10)	-8(16)	30(17)
O(1)	-414(5)	-430(6)	9757(10)	30(4)	48(5)	64(16)	-17(7)	8(12)	20(16)
O(2)	226(6)	-5(7)	10280(11)	40(4)	63(6)	72(18)	-35(9)	-7(14)	25(18)
O(3)	363(8)	-219(11)	3981(14)	78(8)	160(14)	94(23)	-116(18)	-15(23)	36(31)
O(4)	757(9)	1302(7)	3148(13)	140(11)	47(7)	61(19)	58(16)	-44(25)	13(19)
O(5)	1704(7)	50(10)	3277(12)	64(7)	140(13)	83(22)	109(16)	-21(20)	-42(28)
O(6)	1255(6)	742(7)	5266(11)	54(5)	70(7)	65(18)	-38(10)	-47(16)	46(19)
O(7)	-443(7)	-304(8)	6109(13)	54(5)	92(9)	95(21)	-46(11)	-14(17)	-38(23)
O(8)	-1833(6)	-444(8)	6823(12)	48(5)	65(7)	94(20)	16(11)	-9(16)	17(19)
O(9)	-974(7)	-1814(7)	6825(13)	61(6)	47(6)	96(20)	16(11)	26(18)	10(18)
O(10)	-1417(5)	-1147(7)	4681(10)	32(4)	72(6)	41(16)	1(9)	21(12)	33(16)
O(11)	4247(6)	2021(8)	9750(15)	35(4)	84(7)	158(24)	18(10)	3(18)	3(23)
O(12)	3072(7)	2708(8)	8702(13)	52(5)	74(8)	138(22)	53(11)	-3(19)	-41(23)
O(13)	2879(6)	1780(8)	10718(13)	51(6)	72(8)	143(23)	-33(10)	-3(20)	22(24)
O(14)	3598(6)	3306(6)	10816(13)	46(5)	43(5)	154(21)	-16(9)	-30(17)	-48(19)
O(15)	4435(6)	2438(7)	4487(12)	42(5)	75(7)	114(22)	26(10)	-1(17)	4(22)
O(16)	3481(7)	3617(7)	5457(14)	64(6)	53(6)	169(24)	23(11)	-38(21)	-45(21)
O(17)	3005(6)	2120(7)	4522(12)	38(4)	62(7)	105(21)	7(9)	-22(15)	18(19)
O(18)	3781(7)	2107(9)	4572(12)	52([illegible])	95(9)	78(21)	89(13)	-3(20)	25(23)

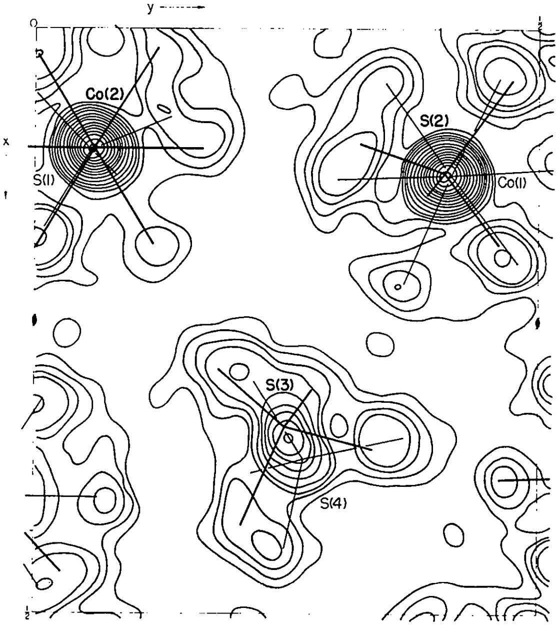

Fig. 1. The electron-density projection down the c axis, calculated at the conclusion of the refinement. Contours are at 4, 6, 8, 10, 15, 20, 25... e.Å^{-2}.

Table 4. *Positional parameters chosen for the hydrogen atoms*

All values have been multiplied by 10^3. The hydrogen atoms were assigned isotropic temperature factors, $B=2{\cdot}0$ Å^2.

		x	y	z			x	y	z
N(1)	H(1)	−183	−35	890	N(7)	H(19)	172	6	1110
	H(2)	−250	−41	998		H(20)	198	−63	989
	H(3)	−197	39	994		H(21)	232	28	1013
N(2)	H(4)	−130	−185	889	N(8)	H(22)	41	170	761
	H(5)	−88	−244	999		H(23)	5	82	734
	H(6)	−177	−237	993		H(24)	−27	127	855
N(3)	H(7)	−154	67	1176	N(9)	H(25)	230	78	802
	H(8)	−130	6	1289		H(26)	168	103	704
	H(9)	−66	47	1199		H(27)	187	173	809
N(4)	H(10)	−232	−194	1173	N(10)	H(28)	58	−94	809
	H(11)	−197	−145	1290		H(29)	102	−40	706
	H(12)	−254	−89	1212		H(30)	145	−95	809
N(5)	H(13)	−10	−190	1162	O(7)	H(31)	−12	−30	530
	H(14)	−24	−116	1269					
	H(15)	−77	−198	1267	O(11)	H(32)	425	143	950
N(6)	H(16)	151	193	1024	O(18)	H(33)	352	236	750
	H(17)	68	207	1002					
	H(18)	87	142	1114					

is 1·6. The observed structure factors, their standard deviations, and the calculated structure factors and phase angles are given in Table 2. The final parameters and their standard deviations, calculated in the usual way from the least-squares residuals, are given in Table 3; since the refinement was by block matrix, the derived e.s.d.'s are slightly underestimated. The coordinates assigned to the hydrogen atoms are given in Table 4. An electron-density projection down the *c* axis, calculated at the conclusion of the refinement, is shown in Fig. 1; a three-dimensional difference map calculated at the same time had no positive peak greater than 0·77 e.Å^{-2} and no negative peak greater than $-0{\cdot}63$ e.Å^{-2}.

The standard deviations in the positional parameters are about 0·003, 0·005, 0·02, and 0·02 Å for the Co, S, O, and N atoms, leading to e.s.d.'s of about 0·02 Å for the distances between the heavy atoms and their ligands and of about 0·03 Å between pairs of lighter atoms; the e.s.d.'s for the bond angles at the heavy atoms are about 2°. The agreement we find among the many independent Co–N and S–O distances and among the N–Co–N angles is within these experimental uncertainties; however, additional uncertainties introduced by our lack of detailed information concerning the effects of thermal motion, particularly of the sulfate and bisulfate groups, suggest that the e.s.d.'s in the interatomic distances should be increased by 50% or so.

Description and discussion of the structure

The cation

Of primary interest in this investigation was the configuration of the O_2 bridge between pairs of cobalt atoms. In contrast to the prediction of Vlček (1960) and the observation of Vannerberg & Brosset (1963) that the O–O bond is perpendicular to the Co–Co axis, we find the arrangement to be a staggered one (Fig. 2). Each cobalt atom is bonded to only one of the bridging oxygen atoms, the average Co–O distance being 1·89 Å and the Co–O–O angle being 118°. The O–O distance, 1·31 Å, is close to that found in superoxides but much shorter than the value 1·48 Å usually found in peroxides (see *e.g.*, Pauling, 1960, pp. 351–2). The five nitrogen atoms on each cobalt atom complete nearly regular octahedra, and the overall symmetry of the cation is approximately C_{2h}. Bond distances and angles within the cation are given in Tables 5 and 6.

We think it appropriate to point out how well the structural details of the cation can be explained on the basis of Pauling's valence-bond theory (Pauling, 1960). The most important valence-bond structure is undoubtedly that shown in Fig. 3; it involves a single bond

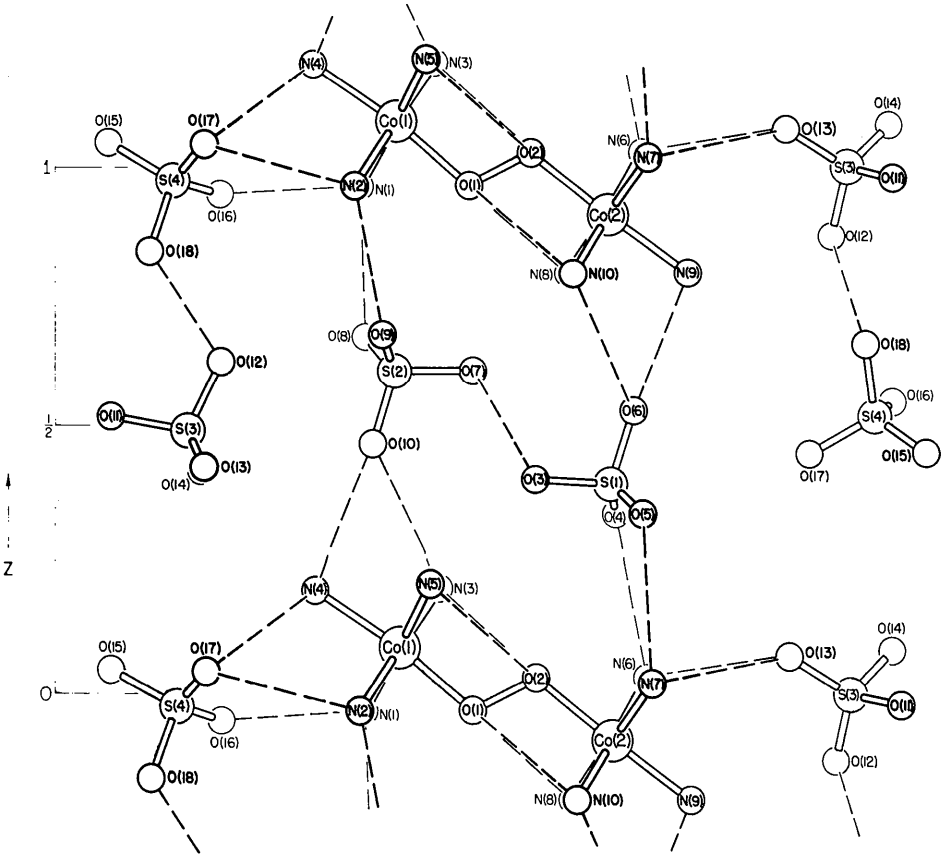

Fig. 2. A section of the structure parallel to the (230) plane. Dashed lines represent probable hydrogen bonds.

Table 5. *Interatomic distances within the ions*

These distances were calculated from the coordinates listed in Table 3 and contain no corrections for thermal motion (see text).

Co(1)–O(1)	1·894 Å	Co(2)–O(2)	1·894 Å
–N(1)	1·903	–N(6)	1·931
–N(2)	1·958	–N(7)	1·955
–N(3)	1·933	–N(8)	1·947
–N(4)	1·969	–N(9)	1·946
–N(5)	1·968	–N(10)	1·951
O(1)–O(2)	1·312	Co(2)···O(1)	2·771
Co(1)···Co(2)	4·562	Co(1)···O(2)	2·775
S(1)–O(3)	1·483	S(2)–O(7)	1·563
–O(4)	1·421	–O(8)	1·428
–O(5)	1·434	–O(9)	1·448
–O(6)	1·431	–O(10)	1·479
S(3)–O(11)	1·535	S(4)–O(15)	1·461
–O(12)	1·478	–O(16)	1·438
–O(13)	1·442	–O(17)	1·460
–O(14)	1·456	–O(18)	1·566

Table 6. *Bond angles*

In each group are listed three atoms, A, B, and C, and the angle ABC.

O(1)—Co(1)-	N(1)	85·7°	O(2)—Co(2)-	N(6)	86·0°
	N(2)	86·6		N(7)	87·0
	N(3)	91·7		N(8)	92·7
	N(4)	176·4		N(9)	178·0
	N(5)	94·1		N(10)	92·6
N(1)	N(2)	89·5	N(6)	N(7)	87·6
	N(3)	90·7		N(8)	89·7
	N(4)	91·0		N(9)	92·9
	N(5)	178·8		N(10)	177·2
N(2)	N(3)	178·3	N(7)	N(8)	177·3
	N(4)	92·1		N(9)	91·3
	N(5)	89·3		N(10)	89·9
N(3)	N(4)	89·6	N(8)	N(9)	89·0
	N(5)	90·5		N(10)	92·9
N(4)	N(5)	89·3	N(9)	N(10)	88·4
Co(1)-O(1)—	O(2)	117·8	Co(2)-O(2)—	O(1)	117·5
O(3)—S(1)—	O(4)	109·2	O(7)—S(2)—	O(8)	106·0
	O(5)	106·3		O(9)	104·8
	O(6)	108·1		O(10)	106·6
O(4)	O(5)	110·0	O(8)	O(9)	111·0
	O(6)	114·3		O(10)	114·6
O(5)	O(6)	108·6	O(9)	O(10)	113·0
O(11)-S(3)—	O(12)	104·9	O(15)-S(4)—	O(16)	116·4
	O(13)	111·4		O(17)	109·2
	O(14)	102·8		O(18)	103·9
O(12)	O(13)	111·4	O(16)	O(17)	113·0
	O(14)	111·5		O(18)	108·0
O(13)	O(14)	114·2	O(17)	O(18)	105·4

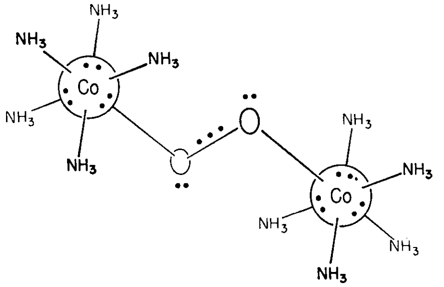

Fig. 3. A valence-bond representation of the cation.

plus a three-electron bond between the oxygen atoms. It leads to formal charges of -3 on Co, $+\frac{1}{2}$ on O and $+1$ on the ammonia groups; however, the ionic character of the various bonds reduces these values to approximately 0, 0, and $+\frac{1}{2}$, respectively (Pauling, 1960, pp. 172–3). The charge on the ammonia groups is presumably distributed equally among the protons.

By sharing electron pairs with six ligands, the cobalt atoms attain a rare gas configuration. In addition, this description explains satisfactorily the following:

(1) The Co–N and Co–O distances, 1·95 (average) and 1·89 Å; the sums of the single-bond radii are 1·95 and 1·91 Å.

(2) The O–O distance, 1·31 Å; this is in satisfactory agreement with the distance predicted for a single bond plus a three-electron bond.

(3) The planarity of the Co–O–O–Co group; this is required by the use of two orbitals of each oxygen atom in forming the O–O bond. In contrast, the O–O bond in H_2O_2 uses but one orbital of each oxygen atom and the molecule is non-planar.

(4) The octahedral coordination about the cobalt atoms; this is due to $3d^24s4p^3$ hybridization. The Co–O–O angles, 118°, are slightly smaller than the predicted value of 125°.

The sulfate groups

The S–O bond distances and O–S–O bond angles are given in Tables 5 and 6. The three longest S–O bonds, S(2)–O(7), S(3)–O(11), and S(4)–O(18), presumably involve OH groups of the three bisulfate ions; in each case an oxygen atom of a neighboring ion is in an appropriate position to accept a hydrogen bond from the OH group. For the remaining thirteen S–O bonds the average distance is 1·45 Å, with an average deviation of 0·016 Å. This distance is somewhat shorter than those found in recent determinations of crystal structures of sulfates (see *e.g.* Baur, 1964). It is quite probable that this apparent shortening is due to the effect of thermal librations; indeed, as we shall discuss later, it appears that the thermal motion of the sulfate group is so large as to require a correction of about 0·05 Å in the S(1)–O(3), S(1)–O(4), and S(1)–O(5) bond distances.

It is perhaps significant that the longest S–O bond in the sulfate ion, S(1)–O(3), is to the oxygen atom which accepts the shortest, and presumably the strongest, hydrogen bond of the structure: O(7)–O(3), 2·50 Å.

Within the bisulfate groups, the O–S–O angles involving the long S–O(H) bond are systematically smaller than tetrahedral. The effect of this distortion is to equalize the non-bonded O···O distances (Donohue, 1965). The average such O···O distance is 2·41 Å, with an average deviation of 0·03 Å.

The arrangement of the ions

The Co–Co axes of the cations are inclined to the *ab* plane at an angle of about 30° and lie nearly parallel to the (230) and ($\bar{2}$30) planes; a section through the plane of the cation is shown in Fig. 2. Directly above (in the **c** direction) and below each cobalt atom lies a sulfur atom of a sulfate or bisulfate group, the sulfate, S(1), lying above Co(2) and a bisulfate, S(2), above Co(1). A pair of N–H···O hydrogen bonds connects each cobalt group to the sulfate or bisulfate groups above and below to form a continuous chain of alternating cations and anions; within the chain, the bisulfate group is bonded to the sulfate group through a strong (2·50 Å) O(7)–H···O(3) hydrogen bond.

The complete structure, viewed down the *c* axis, is shown in Fig. 4. The chains of alternating cobalt and sulfur atoms form, in projection, a hexagonal, graphite-like array. In the centers of the hexagons lie the bisulfate ions S(3) and S(4), bonded together in pairs by the O(18)–H···O(12) hydrogen bond, 2·56 Å long. These pairs of bisulfate ions accept hydrogen bonds from several neighboring cations and donate a hydrogen bond, O(11)–H···O(3), to the sulfate group.

The dashed lines in Fig. 4 represent our choice as to the most probable hydrogen bond arrangement; it is

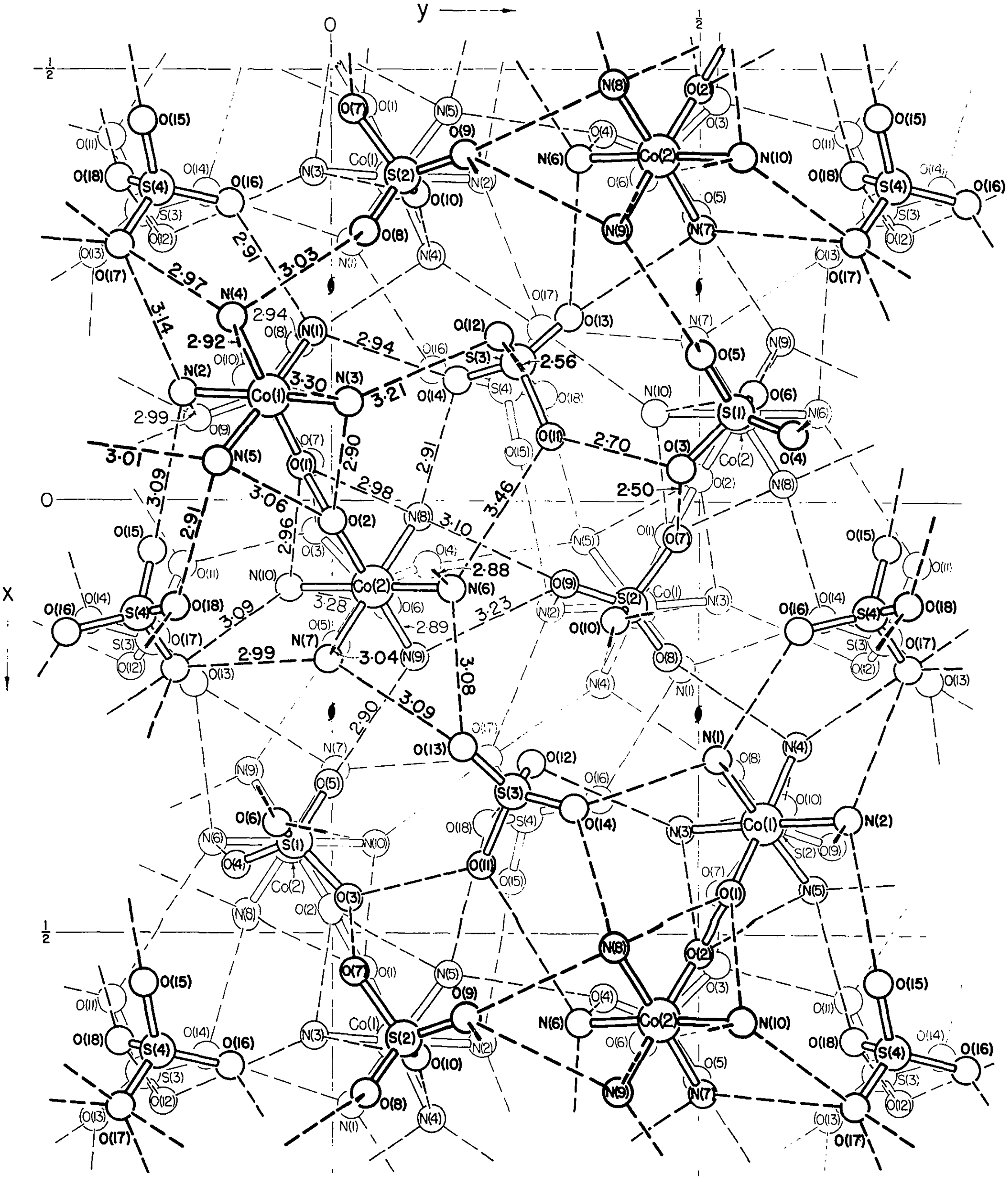

Fig. 4. The structure viewed down the *c* axis. The dashed lines and interatomic distances represent the hydrogen-bond arrangement which we propose. Additional short interionic contacts are listed in Table 7.

the arrangement upon which the coordinates of the hydrogen atoms (Table 4) are based. It seems generally satisfactory in that no H···H distance (except within a given ammonia group) is less than 2·0 Å and each of the 33 hydrogen atoms points more or less in the direction of an oxygen acceptor; however, some of the N–H···O distances are so long (3·46 Å, for example) as to suggest little or no interaction. In Table 7 are listed additional N···O and O···O distances from which alternative, but to our eyes less satisfactory, hydrogen bonding arrangements may be derived. In some cases it appears that a single proton may be shared by two acceptor oxygen atoms to form a bifurcated hydrogen bond, but we have not indicated these possibilities.

The hydrogen-bonding arrangement we propose also includes four N–H···O hydrogen bonds within the cation, two to each oxygen atom, which may lead to additional stability of this group.

Table 7. *Additional non-bonded distances less than* 3·5 Å *and not ascribed to hydrogen bonds*

The atoms in the first column are those whose coordinates are given in Table 3.

From	To	At	Distance
N(6)	O(9)	$\bar{x}, \frac{1}{2}+y, \frac{3}{2}-z$	3·06 Å
	O(10)	$\bar{x}, \frac{1}{2}+y, \frac{3}{2}-z$	3·18
N(7)	O(5)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·07
	O(6)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·26
	O(18)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·33
N(8)	O(6)	x, y, z	3·34
	O(7)	x, y, z	3·00
	O(15)	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	3·40
N(9)	O(12)	x, y, z	3·10
	O(13)	x, y, z	3·37
N(10)	O(7)	x, y, z	3·04
	O(13)	$\frac{1}{2}-x, \bar{y}, -\frac{1}{2}+z$	3·32
	O(15)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·09
N(1)	O(8)	$-\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·00
	O(10)	$-\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·27
N(2)	O(4)	$\bar{x}, -\frac{1}{2}+y, \frac{3}{2}-z$	3·24
	O(6)	$\bar{x}, -\frac{1}{2}+y, \frac{3}{2}-z$	3·11
N(3)	O(3)	$x, y, 1+z$	3·24
	O(8)	$-\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·29
	O(16)	$-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$	3·03
N(4)	O(14)	$\bar{x}, -\frac{1}{2}+y, \frac{5}{2}-z$	3·23
	O(16)	$\bar{x}, -\frac{1}{2}+y, \frac{3}{2}-z$	3·30
N(5)	O(3)	$x, y, 1+z$	2·99
	O(10)	$x, y, 1+z$	3·07
	O(11)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·38
	O(15)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·33
O(1)	O(14)	$-\frac{1}{2}+x, \frac{1}{2}-y, 2-z$	3·42
	O(15)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·24
O(3)	O(10)	x, y, z	3·26
O(6)	O(7)	x, y, z	3·25
O(7)	O(11)	$\frac{1}{2}-x, \bar{y}, -\frac{1}{2}+z$	3·38
	O(16)	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	3·33
O(8)	O(12)	$\bar{x}, -\frac{1}{2}+y, \frac{3}{2}-z$	3·32
	O(16)	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	3·45
O(11)	O(18)	x, y, z	3·26

The thermal motions

Since we applied only approximate corrections for absorption and neglected altogether the corrections for anomalous dispersion, the absolute values of the temperature factors are of doubtful significance*, but the overall pattern of thermal motions we have found is very reasonable.

The Co and S atoms show moderately small and isotropic thermal motions, with r.m.s. amplitudes along the principal directions ranging from 0·17 to 0·25 Å. The motions of the cobalt ligands are slightly greater (and more uncertain), ranging up to 0·29 Å; the maximum amplitudes are in directions approximately perpendicular to the cobalt–ligand bonds. The oxygen atoms of the bisulfate ions show still larger motions, ranging up to 0·37 Å for O(18); here, too, the major axes are oriented perpendicular to the S–O bonds. Three oxygen atoms of the sulfate group show extreme anisotropy, the principal amplitudes of motion being 0·45, 0·45, and 0·43 Å for O(3), O(4), and O(5). Interestingly, the major axes all lie within 20° of the tangents to the circle defined by these three atoms, that is, approximately in the directions expected if the sulfate group were undergoing rigid-body libration about the S(1)–O(6) axis. The r.m.s. amplitude of this implied libration is about 14°, and to correct for its effect these three S–O distances should probably be increased by about 0·05 Å over the values listed in Table 5. Smaller corrections might also be in order for the remaining S–O, Co–N, and Co–O distances, but in view of the relatively high uncertainties in the temperature factors of the lighter atoms, we are reluctant to make them explicitly.

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* The b_{33} terms in particular may be subject to systematic error in view of our difficulties in obtaining accurate interlayer scaling factors.