The minimum intermolecular packing distance (excluding hydrogen atoms) is 3.54 Å between O_1 and C_3 in the molecule directly above the asymmetric portion of the unit cell.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA 95616, AND CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA 91109

The Structure of Decaammine-μ-peroxo-dicobalt Disulfate Tetrahydrate[1]

BY WILLIAM P. SCHAEFER[2]

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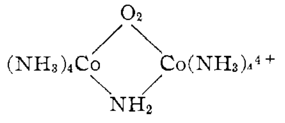
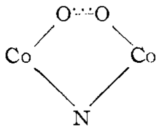
Decaammine-μ-peroxo-dicobalt disulfate tetrahydrate, $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2 \cdot 4H_2O$, a red-brown, diamagnetic salt, crystallizes in the monoclinic space group $P2_1/n$ with $a = 7.62$, $b = 29.72$, $c = 9.60$ Å, and $\beta = 96.97°$; there are four formula units in the cell. The measured density is 1.74 g/cm^3, the calculated density is 1.80 g/cm^3. The structure was solved by Patterson and Fourier techniques and refined by three-dimensional least-squares calculations, based on 2760 reflections collected on a Picker automatic diffractometer, to a final R index of 0.065. The coordinating ligands about the cobalt atoms form nearly regular octahedra with Co–N distances of 1.96 Å and Co–O distances of 1.88 Å. The bridging O–O group is a peroxide ion, with an O–O distance of 1.47 Å and a torsion angle of 146° about the O–O bond. The Co–O–O angles are 113°. The dimensions of the bridging group and the configuration of the cation are markedly different from those found for the paramagnetic, oxidized form of this compound.

Introduction

The structures of the peroxo-bridged dicobalt compounds have been speculated upon since their discovery and characterization by Werner[3] and others. Two series of these compounds are known, the one consisting of green, paramagnetic compounds and the other of red-brown diamagnetic compounds. The cobalt atoms may be joined by one, two, or three bridges, the bridging groups including, besides peroxo and superoxo ions, hydroxo, amido, nitrito, and sulfato groups. The questions of the molecular and electronic structures of these ions have been most recently reviewed by Goodman, Hecht, and Weil;[4] at the time of that review no reliable X-ray structure for any of these compounds was available. Since then, we have determined the structure of the paramagnetic peroxo-bridged ion shown in Figure 1.[5] We have made the point that the structural details of the cation can be well explained by Pauling's valence-bond theory, with the bridging group being considered a superoxide ion. This formulation was not original with us,[6] but it leads to some interesting predictions as to the structures of other compounds of this sort. For example, consider the paramagnetic ion



Because the single bond plus the three-electron bond joining the two oxygen atoms require the use of two orbitals, the entire



grouping is expected to be planar. Recently, the structure of this ion has been determined,[7] and the five central atoms are in fact nearly coplanar. As in the case of the singly bridged compound, the O–O bond distance, 1.31 Å, is typical of a superoxide group.

If the paramagnetic ions are considered to be derivatives of the superoxo ion,[8] then the addition of an electron to give the diamagnetic species should lead to a peroxo derivative. The two oxygen atoms are now joined by only a single bond, and this bond length should be near 1.48 Å; the O–O distance found in H_2O_2 is 1.47 Å,[9] and in BaO_2 it is 1.49 Å.[10] Furthermore, the Co–O–O–Co grouping should now not be planar; the torsion angle about the O–O bond in H_2O_2 is about 90°,[11] and a torsion angle is to be expected in the cobalt compound as well. This paper reports the structure of the compound decaammine-μ-peroxo-dicobalt disulfate tetrahydrate; the basic structure of the cation is as we have predicted. Our structure differs from the one reported by Vannerberg[12] for the μ-peroxo-dicobalt

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[1] Contribution No. 3548 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology. This work was supported in part by NSF Grant GP-5768.

[2] University of California, Davis, Calif. Work done at Davis.

[3] A. Werner, *Ann.*, **375**, 1 (1910).

[4] G. L. Goodman, H. G. Hecht, and J. A. Weil in "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962.

[5] W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, **21**, 735 (1966).

[6] J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953).

[7] G. G. Christoph, R. E. Marsh, and W. P. Schaefer, to be published.

[8] Members of the paramagnetic series should properly by named "μ-superoxo," but the original designation of "peroxo" for both kinds of ions seems likely to remain.

[9] P. A. Giguère and V. Schomaker, *J. Am. Chem. Soc.*, **65**, 2025 (1943).

[10] S. C. Abrahams and J. Kalnajs, *Acta Cryst.*, **7**, 838 (1954).

[11] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **42**, 3054 (1965). These authors comment that the torsion angle is very sensitive to the environment of the molecule.

[12] N.-G. Vannerberg, *Acta Cryst.*, **18**, 449 (1965).

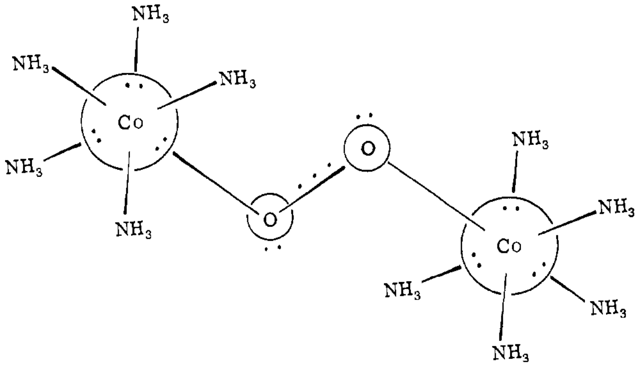

Figure 1.—The decaammine-μ-superoxo-dicobalt(+5) cation.

cation (studied as the tetrathiocyanate) in which he found the Co–O–O–Co grouping to be planar. (These four atoms lay in a crystallographic mirror plane.) Vannerberg also observed a very long (1.65-Å) O–O distance. It may be noted that Vannerberg found some of the thiocyanate ions to be disordered and that his final R index was 0.16, an unsatisfactory value. Because no disorder was found in the present study and because of the substantially better agreement between observed and calculated structure factors, we feel confident that the description given here for the diamagnetic μ-peroxo-dicobalt cation is the correct one.

Experimental Section

The μ-peroxo-dicobalt(+4) ion is the first product of the reaction between oxygen and cobalt(II) ions in strongly ammoniacal solutions.[13] Charles and Barnartt[14] were able to obtain crystals of decaammine-μ-peroxodicobalt disulfate *tri*hydrate by oxidizing a solution of cobalt sulfate in ammonia and then cooling it. We found that cooling the solution before bubbling air through it enabled us to make good crystals of the sulfate, but as the tetrahydrate. Fourteen grams of cobalt sulfate hexahydrate was dissolved in 200 ml of water and cooled in ice; 100 ml of cold, concentrated ammonia was added and air was slowly bubbled in through a sintered-glass disk for 1.5 hr. The resulting red-brown crystals were filtered, washed with ethanol and ether, and stored in tightly stoppered bottles without further drying. Attempts were made to recrystallize the material from acids, bases (including ammonia), or water. Nothing worked; the compound always decomposed, giving off oxygen and leaving various Co(II) species behind. We therefore were forced to use the material as prepared. The sulfate thus formed, however, is much more stable toward air oxidation than is decaammine-μ-peroxo-dicobalt tetranitrate; crystals of the sulfate can be left in the open for days before they turn green, whereas the nitrate begins to be oxidized in several hours. On the other hand, bottles containing the sulfate compound always smelled strongly of ammonia, so that some spontaneous decomposition of the complex evidently takes place. This may be the reason that the measured density is so low; at any rate, it discouraged us from performing any analyses on the material. The satisfactory solution of the structure confirms our formulation as $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2 \cdot 4H_2O$. The crystal data for this compound are collected in Table I, including the density as measured by displacement of ethanol.

Table I

Crystal Data for Decaammine-μ-peroxo-dicobalt Disulfate Tetrahydrate

$Co_2S_2O_{14}N_{10}H_{38}$	Mol wt 584.36
Space group $P2_1/n$	$F(000) = 1224$
	$z = 4$
$a = 7.614\ (2)$ Å[a]	$T = 22°$
$b = 29.672\ (5)$ Å	Co $K\alpha_1 = 1.78892$ Å
$c = 9.595\ (1)$ Å	Co $K\alpha_2 = 1.79278$ Å
$\beta = 96.97\ (1)°$	
$d_m = 1.74\ (3)$ g/cm^3	$d_x = 1.80$ g/cm^3

[a] Figures in parentheses here and in other tables are estimated standard deviations in the last digit. The unit cell esd's were obtained from a least-squares fit of 2θ values of eight high-angle reflections measured on the diffractometer, both Co $K\alpha_1$ and α_2 eaks being used for all eight reflections.

Unit cell dimensions were measured and intensity data collected on an automated Picker diffractometer using cobalt radiation, an iron oxide filter, and a θ–2θ scan. No attenuators were required for any reflection. Background was counted for 40 sec at both ends of the scan. All of the reflections of the type $\pm h,k,l$ (or their Friedel equivalents) accessible below $2\theta = 165°$ were scanned at 1°/min, the scan range being from 1° below the 2θ value calculated for $K\alpha_1$ radiation to 1° above the 2θ value calculated for $K\alpha_2$ radiation. The take-off angle used was 3°. The space group $P2_1/n$ was chosen because of the very low intensity of all reflections $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$). The general equivalent positions in $P2_1/n$ are $\pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. The crystal used was a fragment 0.09 × 0.11 × 0.18 mm, cut from a needle and completely coated with epoxy mounting cement so as to retard any air oxidation of the crystal. The 0.18-mm direction corresponded to the a axis. This axis was roughly coincident with the spindle axis, but the crystal was deliberately misoriented by about 20° before being placed on the diffractometer. A single reflection (0, 20, 0) was measured periodically during the 10 days required to collect the data; the counts from this reflection decreased continually during that time, from about 6600 (corrected for background) to 5600, or about 15%. This decrease implied a decomposition in the crystal which was not unexpected, in view of the ease with which the material is air-oxidized and its over-all low chemical stability. In an attempt to correct for this, the reflections were divided into 15 equal groups sequentially. The measured counts in the first group were multiplied by 1.00, in the second by 1.01, in the third by 1.02, etc. These new values of the observed counts were then corrected for background, and Lorentz and polarization corrections were applied. No corrections were made for absorption; the linear absorption coefficient for Co $K\alpha$ radiation is 68.5 cm^{-1}, and neglect of the absorption correction could have caused errors of up to 20% in the relative values of F. (One attempt to grind a sphere from a good-sized chunk of the compound gave a powder; the project was abandoned.) Reflections for which I was calculated to be negative were assigned a value of F (and a weight) = 0; all the reflections which were measured above 0 were treated as observed. The standard deviations of the structure factors were calculated after the manner of Busing and Levy.[15] The constant d in our formula

$$\sigma^2(I) = S + (B_1 + B_2)\frac{t}{80} + (dS)^2$$

was chosen to be 0.005; this reflects previous experience with the Picker instrument.[16] (S = counts in scan, $B_1 + B_2$ = counts in background, and t = time for scan.) Data were collected for 2846 independent reflections, of which 2318 were more than two standard deviations above the background.

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(13) M. Mori and J. A. Weil, *J. Am. Chem. Soc.*, in press.

(14) R. G. Charles and S. Barnartt, *J. Inorg. Nucl. Chem.*, **22**, 69 (1961).

(15) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(16) A referee has kindly pointed out an error in the equation used for this calculation; the second term of course should have been $(B_1 + B_2) \cdot (t/80)^2$. This mistake caused the weights of the weaker reflections to be higher than they should have been; the error in the weights varies from +18% at $F = 0$ to 0 at $F = 100$. In view of the fact that these statistical weights were corrected in the final stages of the refinement to further downweight the strong reflections, the original mistake was not considered serious enough to warrant repeating all the calculations.

Determination and Refinement of the Structure

The cobalt positions were easily found from a three-dimensional sharpened Patterson map; a three-dimensional electron density map based only on the cobalt atoms indicated the two sulfate groups, and a second electron density map phased on the cobalt atoms and the sulfate ions revealed all of the remaining nonhydrogen atoms. A structure-factor calculation at this point gave an R index of 0.36 $(R = \Sigma|F_o - |F_c||/\Sigma F_o)$; four cycles of full-matrix least squares, varying in a single matrix the scale factor, positional parameters for all nonhydrogen atoms, anisotropic temperature factors for the four heavy atoms, and isotropic temperature factors for the lighter ones (133 parameters), reduced the R index to 0.11 and confirmed the trial structure.

Calculations were done on an IBM 7040 machine using programs written by Professor H. Hope and Dr. A. T. Christensen; the least-squares program was one by Gantzel, Sparks, Long, and Trueblood. The final refinement was done on an IBM 7094 computer using the CRYRM crystallographic computing system.[17] Form factors for Co, S, O, and N were taken from the "International Tables,"[18] the values for cobalt being reduced by 2.19 electrons to take account of anomalous dispersion.[19] Form factors for hydrogen were taken from Stewart, Davidson, and Simpson.[20] The weights used for the least-squares refinement were taken as $1/(\sigma^2(F_o^2))$ as calculated during the initial data processing; these weights were later multiplied by the function $1/(1 + 0.0085F_o)$. This correction was made because the value of the goodness of fit was very high and it appeared to us that the strong reflections should be down-weighted. The correction was chosen to approximate the result we would have obtained had we assigned a value of 0.02, rather than 0.005, to d in our formula for $\sigma^2(I)$. The quantity minimized in the final least-squares calculations was $\Sigma w(F_o^2 - F_c^2)^2$.

At this point in the refinement, electron density maps were calculated in the planes where the ammine hydrogen atoms were expected, and these 30 hydrogen atoms were included in the succeeding structure factor calculations; neither their coordinates nor their temperature factors were ever refined. The eight hydrogen atoms attached to the oxygen atoms of the water molecules were similarly positioned and the refinement continued for several more cycles. A total of 253 parameters were refined; the positional parameters of all of the nonhydrogen atoms were included in one matrix and their anisotropic temperature factors and a scale factor in another. Nine reflections which appeared to be suffering from secondary extinction—110, 020, 130, 040, 140, 160, $\bar{1}01$, 101, and 041—were given zero weight for all the remaining calculations. The refinement proceeded smoothly for all atoms except O(7), O(9), and O(10). These atoms had very large anisotropic temperature factors and the sulfate group they formed with S(2) and O(8) was rather distorted. No error could be found to account for this so the effect was judged to be real, and the refinement was continued for three cycles after a final adjustment (by difference maps) of the positions of the hydrogen atoms. The maximum shift of any parameter in the final cycle was 0.6 times its standard deviation.

The final R index for 2760 reflections of nonzero weight was 0.065 and the goodnesss of fit, $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, is 2.1. The final weighted R index is 0.012. A final difference map showed one excursion of +1.5 electrons and no others greater than $|0.7|$ electron. The observed and calculated structure factors are given in Table II. The final parameters of the nonhydrogen atoms and their standard deviations are listed in Table III; because the final refinement was by block matrix, the derived esd's are slightly underestimated. The coordinates assigned to the hydrogen atoms are given in Table IV; all of the hydrogen atoms were assigned isotropic temperature factors with $B = 3.5$ Å^2. The standard deviations in the positional parameters are about 0.001 Å for the cobalt atoms, 0.002 Å for the sulfur atoms, and 0.005 Å for oxygen and nitrogen atoms, leading to esd's of about 0.005 Å for distances between heavy atoms and their ligands and 0.007 Å for distances between light atoms; the esd's for the bond angles at the heavy atoms are about 1°. The agreement we find among the many independent bond distances and angles is approximately in accord with these esd's. None of these esd's applies, of course, to sulfate group 2; here the effects of thermal motion (to be discussed later) are so large as to preclude any accurate interpretation of the calculated bond distances and angles.

Description of the Structure

A. The Cation.—The two cobalt atoms in this cation are joined by a peroxo bridge, the five coordinated nitrogen atoms around each cobalt atom completing nearly regular octahedra. The oxygen–oxygen distance in the bridge is 1.47 Å, exactly the same as is found in H_2O_2. This is in contrast to the situation in the oxidized, paramagnetic form of this cation, in which the O–O distance is 1.31 Å. Moreover, in the reduced form the Co–O–O–Co grouping is grossly nonplanar, the torsion angle about the O–O bond being 146° (see Figures 2 and 3); in the oxidized form these four atoms are nearly coplanar. These features of the bridging group definitely identify this as a peroxo-bridged cation and the oxidized form as a superoxo-bridged species. The only significant differences between the oxidized and the reduced forms are the longer O–O distance and the twisting of the cobalt atoms out of the central plane. Thus it is reasonable to conclude that the oxidation–reduction reaction relating these two cations is essentially the removal or addition of a single electron in the O–O bond; there can be no longer any

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(17) D. J. Duchamp, American Crystallographic Association Meeting, Bozeman, Mont., 1964, Paper B-14.

(18) "International Tables for Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202–205.

(19) $\Delta f'$ was obtained by interpolation from the data given by D. Cromer, *Acta Cryst.*, **18**, 17 (1965). $\Delta f''$ obtained the same way was +0.74; it was neglected because its effect would be small in a centric structure and because our program was not written to include it.

(20) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Table II

Observed and Calculated Structure Factors (Both ×10)[a]

H	0	0
0	---*	2082
2	---*	1238
4	872	930
6	122	-133
H	1	0
1	826*	-868
2	400	407
3	444	-440
4	1116	1206
5	146	119
6	459	-473
7	356	-377
H	2	0
0	461*	482
1	381	-398
2	1262	1342
3	252	-235
4	160	169
5	608	606
6	325	-334
7	155	157
H	3	0
1	1013*	1096
2	228	212
3	442	450
4	650	-668
5	482	504
6	39	-8
7	94	-109
H	4	0
0	706*	-809
1	2199*	2601
2	507	-518
3	345	347
4	97	-16
5	654	-672
6	337	-330
7	210	-191
H	5	0
1	321	-344
2	384	365
3	832	-858
4	413	435
5	271	250
6	333	327
7	343	-351
H	6	0
0	1240	1320
1	752*	-839
2	105	137
3	189	-177
4	621	654
5	48	-61
6	234	-235
7	160	158
H	7	0
1	283	272
2	259	-250
3	488	-514
4	486	-479
5	781	833
6	335	-355
7	135	-129
H	8	0
0	987	1019
1	665	733
2	80	-49
3	225	-231
4	492	-519
5	104	109
6	113	-129
7	241	246
H	9	0
1	617	638
2	523	530
3	345	369
4	627	658
5	164	180
6	530	-559
7	57	66
H	10	0
0	1189	1247
1	197	-188
2	134	-121
3	635	-656
4	80	-91
5	685	-728
6	194	210
7	316	333
H	11	0
1	82	-100
2	256	-272
3	292	-306
4	792	824
5	611	-625
6	324	-321
7	69	31
H	12	0
0	164	-117
1	327	-340
2	162	121
3	255	248
4	511	545
5	210	-208
6	134	132
7	232	260
H	13	0
1	354	-380
2	506	-541
3	440	457
4	---*	17
5	527	-551
6	93	-107
H	14	0
0	360	355
1	150	180
2	618	-641
3	347	368
4	328	-364
5	165	169
6	500	503
H	15	0
1	305	318
2	179	201
3	840	877
4	417	-418
5	540	-523
6	213	209
H	16	0
0	383	-408
1	838	-930
2	396	415
3	---*	29
4	240	-200
5	326	-329
6	323	291
H	17	0
1	751	-774
2	562	560
3	549	-541
4	292	-282
5	97	-65
6	87	94
H	18	0
0	503	-439
1	577	-612
2	443	443
3	639	613
4	545	506
5	198	240
6	60	2
H	19	0
1	264	283
2	226	-230
3	362	-385
4	366	-393
5	238	233
H	20	0
0	1147	1168
1	588	576
2	---*	19
3	332	319
4	596	-635
5	267	237
H	21	0
1	582	580
2	110	-82
3	422	428
4	290	273
5	217	200
6	185	175
H	22	0
0	513	-549
1	134	133
2	709	704
3	130	-131
4	242	-199
5	362	-346
6	117	102
H	23	0
1	523	-508
2	69	-110
3	254	-243
4	376	370
5	225	-238
H	24	0
0	587	555
1	716	686
2	266	269
3	180	-187
4	55	6
5	159	164
H	25	0
1	---*	22
2	52	-28
3	324	308
4	150	-150
5	139	-149
H	26	0
0	358	-339
1	510	485
2	202	-188
3	424	-416
4	338	-335
5	213	217
H	27	0
1	---*	61
2	95	121
3	391	377
4	110	-112
H	28	0
0	415	401
1	72	-58
2	76	102
3	81	-64
4	85	66
H	29	0
1	347	-334
2	138	134
3	65	8
H	30	0
0	401	379
1	98	-83
2	64	-12
3	85	-72
H	31	0
1	77	80
2	180	187
H	32	0
0	504	-509
1	42	9
H	0	1
-7	353	358
-5	209	216
-3	284	267
-1	1455*	1560
1	581*	545
3	374	-388
5	841	864
7	62	-36
H	1	1
-7	273	259
-6	660	-668
-5	578	593
-4	425	447
-3	141	113
-2	1254	1242
-1	534	-498
0	188	-185
1	555	500
2	395	339
3	290	-303
4	795	-785
5	82	-23
6	482	475
7	328	-338
H	2	1
-7	180	184
-6	629	-647
-5	1079	1092
-4	511	518
-3	235	217
-2	16	1
-1	1057	1066
0	674	-642
1	493	-476
2	864	833
3	249	223
4	255	226
5	475	-460
6	338	310
7	188	-204
H	3	1
-7	250	-256
-6	281	268
-5	448	447
-4	580	604
-3	1616	1681
-2	1317	1297
-1	1158	1156
0	430	-470
1	444	440
2	1499	1478
3	295	-288
4	157	-147
5	552	552
6	636	641
7	312	-322
H	4	1
-7	64	44
-6	102	95
-5	242	-268
-4	330	332
-3	191	195
-2	553	556
-1	1446	1487
0	523*	-591
1	504	504
2	452	-443
3	680	673
4	272	-277
5	199	-158
6	834	-797
7	---*	-26
H	5	1
-7	565	-588
-6	461	-457
-5	385	398
-4	491	-523
-3	265	-285
-2	132	161
-1	1358	1408
0	654	-716
1	757	-740
2	962	-925
3	59	75
4	167	-187
5	837	844
6	286	-275
7	23	-42
H	6	1
-7	166	-125
-6	205	-205
-5	575	604
-4	121	-94
-3	483	509
-2	1117	1159
-1	137	144
0	477	472
1	2001	2109
2	951	-973
3	495	-477
4	166	-143
5	514	502
6	230	-219
7	145	133
H	7	1
-7	121	78
-6	84	-77
-5	120	136
-4	781	-792
-3	419	405
-2	902	-915
-1	490	-489
0	109	144
1	638	619
2	---*	-23
3	226	-220
4	728	740
5	68	-86
6	483	-481
7	525	-525
H	8	1
-7	222	-228
-6	367	-375
-5	97	63
-4	207	197
-3	457	-463
-2	475	489
-1	794	-837
0	1269	1297
1	364	361
2	88	48
3	802	-854
4	298	304
5	126	129
6	71	76
7	---*	18
H	9	1
-7	303	-296
-6	330	326
-5	272	-296
-4	119	-93
-3	54	91
-2	537	571
-1	681	675
0	309	313
1	238	226
2	83	-51
3	235	261
4	295	311
5	456	-464
6	100	64
7	118	108
H	10	1
-7	92	-94
-6	405	390
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1	169	150
2	255	-248
3	53	-25
4	174	158
H	19	6
-5	226	212
-4	150	130
-3	230	266
-2	179	-180
-1	156	-179
0	421	-413
1	245	252
2	93	-57
3	372	-352
4	268	-283
H	20	6
-5	96	-107
-4	454	-442
-3	139	133
-2	27	-7
-1	221	-250
0	347	-359
1	222	216
2	149	-141
3	102	-101
H	21	6
-4	132	131
-3	215	210
-2	179	-171
-1	49	25
0	481	443
1	512	488
2	48	-53
3	209	-205
H	22	6
-4	56	41
-3	141	-135
-2	340	335
-1	172	-162
0	131	-118
1	385	-377
2	156	134
3	67	-32
H	23	6
-4	---*	9
-3	253	-258
-2	225	-244
-1	347	-326
0	246	263
1	76	-50
2	464	-492
H	24	6
-3	152	122
-2	107	-177
-1	123	100
0	344	379
1	170	187
2	42	-17
H	25	6
-3	---*	29
-2	257	-253
-1	125	103
0	142	147
1	161	-143
H	26	6
-2	373	-388
-1	113	-102
0	54	-40
1	100	125
H	0	7
-5	717	701
-3	328	-313
-1	791	752
1	261	257
3	27	-83
5	209	219
H	1	7
-6	500	-512
-5	96	-65
-4	32	9
-3	119	28
-2	496	-463
-1	706	-650
0	91	-10
1	246	-268
2	173	-146
3	620	-604
4	115	97
5	50	-68
H	2	7
-6	69	35
-5	---*	-18
-4	247	-256
-3	635	-630
-2	898	892
-1	129	-115
0	196	168
1	162	-152
2	855	826
3	---*	54
4	185	175
5	144	136
H	3	7
-6	296	297
-5	94	72
-4	525	535
-3	215	164
-2	501	482
-1	302	-267
0	114	-53
1	167	171
2	205	182
3	98	-106
4	72	-39
5	64	42
H	4	7
-5	211	-226
-4	649	-650
-3	202	-181
-2	640	609
-1	76	-97
0	661	-644
1	197	223
2	318	-308
3	79	-67
4	124	-99
5	76	60
H	5	7
-5	224	196
-4	55	-10
-3	417	-400
-2	590	-552
-1	371	346
0	113	115
1	266	252
2	469	-416
3	458	464
4	229	200
5	75	-102
H	6	7
-5	278	261
-4	187	-150
-3	647	648
-2	657	656
-1	410	-397
0	241	-247
1	380	356
2	93	111
3	65	34
4	108	-28
5	116	-78
H	7	7
-5	173	-159
-4	200	-209
-3	172	-149
-2	419	-385
-1	344	-319
0	688	674
1	333	-327
2	726	-757
3	137	-36
4	317	355
5	179	-198
H	8	7
-6	57	54
-5	264	-246
-4	203	-176
-3	197	162
-2	19	54
-1	746	-738
0	433	437
1	---*	-16
2	506	456
3	233	254
4	41	-95
5	135	-134
H	9	7
-6	312	327
-5	221	-191
-4	49	34
-3	196	157
-2	499	463
-1	249	265
0	64	47
1	405	-416
2	113	75
3	777	750
4	154	-184
5	59	-22
H	10	7
-6	108	105
-5	112	-102
-4	234	-244
-3	101	94
-2	500	-485
-1	165	146
0	39	72
1	116	-76
2	130	-69
3	82	-81
4	309	-323
H	11	7
-6	289	-307
-5	53	9
-4	56	26
-3	193	-149
-2	130	-125
-1	928	866
0	269	-242
1	642	-624
2	381	394
3	725	716
4	110	-110
H	12	7
-6	53	13
-5	215	182
-4	92	-84
-3	159	169
-2	84	35
-1	470	472
0	93	42
1	118	56
2	70	12
3	354	-340
4	65	62
H	13	7
-5	32	-33
-4	103	59
-3	157	-140
-2	29	23
-1	271	-248
0	128	-133
1	271	-260
2	436	416
3	52	-20
4	163	-167
H	14	7
-5	119	-101
-4	80	-31
-3	233	-208
-2	256	231
-1	---*	1
0	116	89
1	216	-220
2	---*	35
3	144	-126
4	113	141
H	15	7
-5	241	238
-4	55	-37
-3	77	8
-2	595	581
-1	169	171
0	185	-169
1	231	193
2	588	581
3	82	-61
4	467	-479
H	16	7
-5	118	-114
-4	218	-229
-3	222	191
-2	---*	14
-1	---*	21
0	329	-326
1	113	-121
2	303	-296
3	---*	18
H	17	7
-5	271	293
-4	170	-198
-3	101	-77
-2	145	-141
-1	208	175
0	336	-306
1	89	87
2	70	39
3	152	-157
H	18	7
-4	136	-122
-3	465	491
-2	352	331
-1	125	99
0	66	10
1	155	145
2	138	164
3	77	-90
H	19	7
-4	87	-45
-3	34	-30
-2	41	-7
-1	430	-453
0	96	52
1	162	-157
2	117	-63
3	455	-466
H	20	7
-4	195	199
-3	65	59
-2	69	18
-1	381	-380
0	85	-82
1	49	5
2	138	139
H	21	7
-3	54	70
-2	275	295
-1	108	119
0	95	84
1	219	205
2	80	-69
H	22	7
-3	318	318
-2	392	-389
-1	344	-322
0	165	-166
1	204	225
H	23	7
-2	181	-187
-1	187	183
0	171	-154
1	121	-88
H	24	7
-1	178	169
0	326	334
H	0	8
-6	113	99
-4	499	508
-2	187	189
0	270	249
2	183	-192
4	229	237
H	1	8
-6	34	40
-5	197	200
-4	77	-86
-3	238	-225
-2	275	-260
-1	346	-319
0	364	-375
1	229	218
2	326	-337
3	564	-594
4	53	-80
H	2	8
-6	285	-307
-5	67	1
-4	56	-10
-3	296	260
-2	71	32
-1	189	-194
0	298	-295
1	473	490
2	71	-69
3	157	142
4	---*	13
H	3	8
-6	168	177
-5	197	194
-4	173	-157
-3	240	219
-2	138	-160
-1	---*	-68
0	241	254
1	297	292
2	362	-358
3	56	-8
4	427	446
H	4	8
-6	188	-188
-5	173	174
-4	123	127
-3	319	-295
-2	120	-104
-1	309	-329
0	86	47
1	399	-383
2	174	-162
3	51	-63
4	113	87
H	5	8
-6	281	301
-5	387	-397
-4	146	-130
-3	52	88
-2	114	121
-1	438	-436
0	865	876
1	5	-13
2	402	-406
3	104	80
4	562	603
H	6	8
-5	213	238
-4	511	525
-3	200	-192
-2	501	-482
-1	99	-87
0	557	568
1	29	-82
2	180	-158
3	118	123
4	118	-117
H	7	8
-5	267	-273
-4	64	-44
-3	123	108
-2	478	-511
-1	190	231
0	193	225
1	156	-147
2	360	-387
3	186	173
4	86	-53
H	8	8
-5	276	287
-4	100	-128
-3	252	-285
-2	490	-461
-1	395	397
0	106	-104
1	139	111
2	110	101
3	80	51
4	173	-161
H	9	8
-5	90	-105
-4	304	318
-3	367	381
-2	305	-309
-1	282	257
0	88	65
1	139	-100
2	107	89
3	247	247
4	105	101
H	10	8
-5	272	281
-4	224	-234
-3	750	-755
-2	289	287
-1	449	468
0	63	-63
1	484	-484
2	109	-84
3	147	-128
H	11	8
-5	80	-83
-4	136	127
-3	146	-128
-2	125	-118
-1	147	-118
0	159	134
1	118	74
2	102	117
3	43	16
H	12	8
-5	177	182
-4	101	129
-3	89	-76
-2	305	322
-1	421	411
0	58	-28
1	112	-109
2	60	81
3	210	223
H	13	8
-5	216	213
-4	59	-37
-3	194	-209
-2	182	-179
-1	133	103
0	99	-19
1	145	133
2	330	-338
3	368	-374
H	14	8
-4	426	-441
-3	93	58
-2	228	203
-1	177	-170
0	---*	-261
1	144	161
2	213	226
3	80	102
H	15	8
-4	97	68
-3	137	90
-2	115	117
-1	190	211
0	---*	314
1	---*	8
2	139	-147
3	99	-91
H	16	8
-4	198	-210
-3	254	-261
-2	209	197
-1	252	-242
0	166	-163
1	252	-262
2	172	147
H	17	8
-3	274	-277
-2	76	18
-1	62	59
0	115	142
1	219	-212
2	306	-309
H	18	8
-3	138	127
-2	---*	-7
-1	152	147
0	398	403
1	229	246
2	119	-107
H	19	8
-3	59	-13
-2	29	14
-1	158	133
0	137	-123
1	272	-282
H	20	8
-2	238	-238
-1	79	-60
0	75	45
1	83	75
H	21	8
-1	278	310
H	0	9
-5	60	89
-3	456	470
-1	150	-92
1	303	283
3	279	-288
H	1	9
-5	296	-306
-4	213	-210
-3	143	128
-2	126	112
-1	577	-582
0	130	-145
1	82	1
2	50	4
3	79	-37
H	2	9
-5	236	-253
-4	251	263
-3	208	218
-2	42	-6
-1	368	-394
0	411	-414
1	35	54
2	102	49
3	113	-101
H	3	9
-5	342	-347
-4	35	-29
-3	241	227
-2	444	440
-1	262	-261
0	205	-215
1	52	44
2	184	186
3	251	256
H	4	9
-5	180	-189
-4	153	146
-3	124	83
-2	540	-536
-1	149	96
0	90	-84
1	69	-69
2	361	-356
3	72	34
H	5	9
-4	105	129
-3	111	106
-2	333	-353
-1	325	280
0	191	-184
1	204	208
2	155	124
3	267	290
H	6	9
-4	166	169
-3	77	46
-2	266	-258
-1	442	460
0	113	58
1	69	8
2	99	-90
3	119	-115
H	7	9
-4	224	235
-3	83	-13
-2	280	-277
-1	500	-500
0	178	181
1	83	42
2	71	47
3	459	-479
H	8	9
-4	267	273
-3	332	-342
-2	220	209
-1	270	253
0	45	-10
1	171	-150
2	200	191
H	9	9
-4	201	223
-3	38	-40
-2	151	131
-1	151	-149
0	25	6
1	393	388
2	46	35
H	10	9
-4	39	22
-3	211	-231
-2	63	-29
-1	92	34
0	514	-532
1	135	-132
2	286	-299
H	11	9
-4	196	-194
-3	115	-115
-2	180	-183
-1	171	141
0	147	154
1	328	338
2	240	-265
H	12	9
-3	162	161
-2	190	175
-1	236	-232
0	123	-64
1	206	206
2	198	217
H	13	9
-3	108	-113
-2	120	-112
-1	323	-315
0	329	334
1	112	-102
H	14	9
-3	220	-234
-2	141	-125
-1	340	-362
0	244	237
1	165	181
H	15	9
-2	278	289
-1	50	-42
0	156	161
1	119	115
H	16	9
-2	411	-428
-1	147	-122
0	243	252
H	0	10
-2	148	-150
0	427	452
H	1	10
-3	100	-93
-2	121	-113
-1	146	141
0	264	-256
1	184	-179
H	2	10
-3	179	184
-2	---*	-11
-1	268	249
0	148	165
1	57	-17
H	3	10
-3	37	2
-2	57	45
-1	252	256
0	96	-90
1	198	-197
H	4	10
-3	111	-106
-2	89	108
-1	39	24
0	87	-95
1	397	-408
H	5	10
-3	196	-191
-2	217	207
-1	123	125
0	42	-30
1	39	-22
H	6	10
-3	91	71
-2	137	104
-1	149	151
0	150	-123
1	52	-46
H	7	10
-2	---*	26
-1	162	121
0	440	-451
H	8	10
-2	84	74
-1	169	-159
0	372	-386
H	9	10
-2	389	406
-1	119	113
0	118	-142
H	10	10
-1	408	-430

[a] An asterisk indicates the reflection was given zero weight in the least-squares calculations. $F(000)$ is correctly 12082 on this scale.

question that both cobalt atoms have a +3 oxidation state in both of these cations.

The observed torsion angle of 146° about the O–O bond is larger than that observed in H_2O_2. The obvious reason for this larger angle is a steric one: the coordinated ammonia groups prevent the cobalt atoms from twisting any further. There are three short N–N distances across the bridge as shown in Figure 2; two of these, N(5)–N(6) (3.720 Å) and N(5)–N(9) (3.783 Å), are less than the N–H···N distance (3.88 Å) one calculates from the van der Waals radii for N and H[21] and the third is about equal to this value. Thus the cobalt

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[21] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

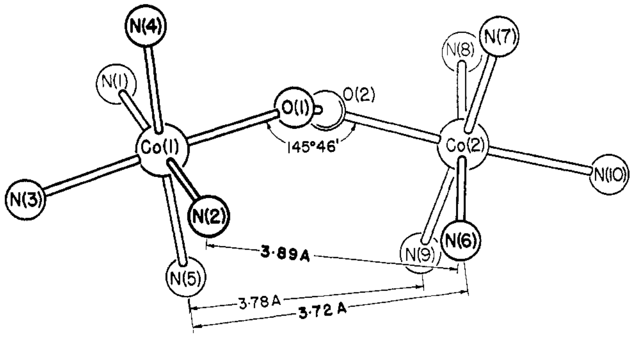

Figure 2.—The decaammine-μ-peroxo-dicobalt(+4) cation.

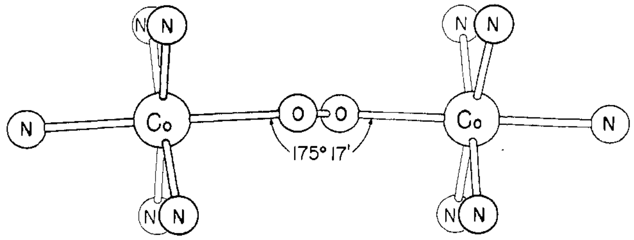

Figure 3.—A view similar to that of Figure 2 of the μ-superoxo-dicobalt(+5) cation.[5]

Table III

Positional and Thermal Parameters of the Nonhydrogen Atoms and Their Standard Deviations[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(1)	3085(1)	751(.3)	1982(1)	83(2)	49(1)	44(1)	-2(1)	13(2)	1(1)
Co(2)	5276(1)	1729(.3)	5222(1)	94(2)	49(1)	54(1)	-4(1)	12(2)	-1(1)
S(1)	7246(2)	4719(.5)	2282(1)	86(3)	54(2)	46(1)	4(1)	18(3)	0(1)
S(2)	7659(2)	1660(.5)	29(2)	106(4)	66(2)	84(2)	-4(1)	0(4)	13(1)
O(1)	3906(5)	1310(1)	2704(4)	135(10)	67(5)	45(4)	-13(3)	35(10)	-4(2)
O(2)	3490(5)	1394(1)	4141(4)	101(9)	81(5)	52(4)	-8(3)	41(10)	-13(3)
O(3)	7179(6)	4389(1)	1133(4)	165(11)	84(6)	64(5)	1(4)	52(12)	-16(3)
O(4)	5734(6)	4636(2)	3084(4)	95(9)	129(7)	71(5)	1(4)	77(11)	-5(3)
O(5)	8906(6)	4679(1)	3231(4)	101(9)	105(6)	74(5)	3(4)	-30(11)	7(3)
O(6)	7092(6)	5180(1)	1708(5)	152(11)	59(5)	104(6)	5(4)	17(13)	9(3)
O(7)	8292(8)	1451(2)	1305(6)	186(14)	394(15)	165(9)	-18(7)	-86(18)	114(6)
O(8)	5743(6)	1613(2)	-324(5)	111(11)	120(7)	122(7)	-2(4)	9(13)	3(4)
O(9)	8200(10)	2095(2)	-123(10)	384(22)	157(10)	546(23)	-90(7)	-283(36)	83(8)
O(10)	8461(9)	1410(3)	-1044(8)	255(18)	642(25)	175(11)	118(11)	11(23)	-64(9)
O(11)	958(7)	2008(2)	2888(7)	200(14)	110(7)	241(11)	25(5)	-193(19)	-31(5)
O(12)	8952(7)	2571(2)	4298(6)	181(13)	154(8)	173(9)	-40(5)	94(17)	-12(4)
O(13)	5361(7)	3594(2)	1673(6)	199(13)	105(7)	162(8)	-16(5)	61(16)	-17(4)
O(14)	2769(6)	4528(2)	990(5)	122(10)	116(6)	85(6)	-11(4)	-19(12)	0(3)
N(1)	899(7)	813(2)	2856(5)	88(11)	85(7)	78(6)	-4(4)	13(13)	-3(3)
N(2)	5720(7)	704(2)	1121(5)	116(11)	60(6)	69(6)	-5(4)	41(13)	4(3)
N(3)	2335(7)	164(2)	1118(5)	139(12)	71(6)	63(6)	-12(4)	46(13)	-2(3)
N(4)	2107(7)	1091(2)	309(5)	136(12)	83(7)	56(6)	7(4)	-4(13)	3(3)
N(5)	4128(7)	439(2)	3666(5)	103(11)	63(6)	57(6)	0(4)	18(12)	-4(3)
N(6)	7138(7)	1422(2)	4359(5)	110(12)	84(7)	83(7)	-5(4)	5(14)	-2(4)
N(7)	5184(7)	2183(2)	3725(5)	117(12)	81(7)	84(7)	-5(4)	-2(14)	7(3)
N(8)	3360(7)	2013(2)	6096(6)	144(13)	84(7)	90(7)	0(5)	36(15)	-12(4)
N(9)	5351(7)	1257(2)	6648(5)	128(12)	66(6)	64(6)	-12(4)	-24(13)	0(3)
N(10)	7034(7)	2101(2)	6409(5)	152(13)	96(7)	59(6)	-16(5)	16(14)	-3(3)

[a] All values except b_{22} have been multiplied by 10^4; b_{22} has been multiplied by 10^5. The temperature factors are of the form $\exp\{-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})\}$.

Table IV

Positional Parameters Assigned to Hydrogen Atoms[a]

		x	y	z			x	y	z
N(1)	H(1)	124	1022	2356	N(6)	H(16)	8196	1420	4941
	H(2)	293	536	2842		H(17)	6830	1122	4140
	H(3)	1140	905	3796		H(18)	7348	1569	3513
N(2)	H(4)	5735	992	966	N(7)	H(19)	6333	2277	3574
	H(5)	6134	539	1698		H(20)	4615	2071	2871
	H(6)	5071	556	246		H(21)	4549	2443	3959
N(3)	H(7)	1292	57	1458	N(8)	H(22)	3040	2298	5671
	H(8)	2111	190	123		H(23)	2322	1834	6000
	H(9)	3224	-55	1315		H(24)	3707	2066	7084
N(4)	H(10)	2759	1351	186	N(9)	H(25)	5647	1373	7558
	H(11)	2101	913	-521		H(26)	4238	1114	6640
	H(12)	924	1183	373		H(27)	6198	1030	6499
N(5)	H(13)	4009	610	4491	N(10)	H(28)	6502	2357	6756
	H(14)	3565	156	3773		H(29)	7570	1938	7185
	H(15)	5371	383	3637		H(30)	7942	2203	5886
O(11)	H(31)	140	1826	2407	O(13)	H(35)	5935	3844	1504
	H(32)	1748	1809	3284		H(36)	4743	3601	2434
O(12)	H(33)	9564	2832	4400	O(14)	H(37)	3712	4568	1609
	H(34)	9612	2388	3834		H(38)	2815	4625	98

[a] All values have been multiplied by 10^4. (All hydrogen atoms were assigned isotropic temperature factors, $B = 3.5$ Å^2.)

Table V

Interatomic Distances within the Ions[a]

Distance	Value, Å	Distance	Value, Å
Co(1)–O(1)	1.876 (7)	Co(2)–O(2)	1.889 (7)
–N(1)	1.961 (9)	–N(6)	1.952 (9)
–N(2)	1.951 (9)	–N(7)	1.966 (9)
–N(3)	1.985 (9)	–N(8)	1.960 (9)
–N(4)	1.964 (9)	–N(9)	1.953 (9)
–N(5)	1.947 (9)	–N(10)	1.981 (9)
Co(1)–Co(2)	4.427 (2)	O(1)–O(2)	1.473 (10)
S(1)–O(3)	1.471 (7)	S(2)–O(7)	1.405 (12)
–O(4)	1.482 (7)	–O(8)	1.464 (9)
–O(5)	1.470 (7)	–O(9)	1.368 (15)
–O(6)	1.474 (8)	–O(10)	1.462 (14)
O(1)–N(1)	2.743 (11)	O(2)–N(6)	2.762 (11)
–N(2)	2.647 (11)	–N(7)	2.728 (11)
–N(4)	2.611 (11)	–N(8)	2.637 (12)
–N(5)	2.744 (11)	–N(9)	2.670 (11)
–N(6)	2.782 (11)	–N(1)	2.791 (11)
–N(7)	2.896 (11)	–N(2)	3.921 (11)
–N(8)	3.930 (12)	–N(4)	3.808 (11)
–N(9)	3.814 (11)	–N(5)	2.920 (11)

[a] These distances were calculated from the parameters listed in Table III and contain no corrections for thermal motion (see text).

atoms seem to have twisted as far as they can without causing primary bond angle distortions.

The average Co–O distance is 1.882 Å, essentially the same as the 1.894 Å found in the superoxo-bridged compounds;[5] the average Co–N distance is 1.962 Å which compares with 1.952 Å found in the superoxo-bridged compounds. There appears to be a slight *trans* effect in this complex: the Co–N bond lengths for the two ammonia groups *trans* to the bridging oxygen atoms are 1.983 Å, whereas the average for the remaining eight Co–N bonds is 1.956 Å. This effect was much less pronounced in the superoxo-bridged cations.

The thermal motions of the cobalt atoms are moderately small and nearly isotropic. The vibrations of the nitrogen and oxygen ligands are somewhat greater, with rms motions along the principal axes ranging from 0.14 to 0.23 Å (see Table VII); in general the maximum amplitudes are in directions roughly perpendicular to the cobalt–ligand bonds.

Table VI

Bond Angles

Angle	Deg	Angle	Deg
O(1)-Co(1)-N(1)	91.2	O(2)-Co(2)-N(6)	91.9
O(1)-Co(1)-N(2)	87.5	O(2)-Co(2)-N(7)	90.1
O(1)-Co(1)-N(3)	175.9	O(2)-Co(2)-N(8)	86.5
O(1)-Co(1)-N(4)	85.7	O(2)-Co(2)-N(9)	88.0
O(1)-Co(1)-N(5)	91.8	O(2)-Co(2)-N(10)	176.5
N(1)-Co(1)-N(2)	178.7	N(6)-Co(2)-N(7)	88.5
N(1)-Co(1)-N(3)	92.6	N(6)-Co(2)-N(8)	177.7
N(1)-Co(1)-N(4)	92.5	N(6)-Co(2)-N(9)	90.1
N(1)-Co(1)-N(5)	88.4	N(6)-Co(2)-N(10)	91.5
N(2)-Co(1)-N(3)	88.7	N(7)-Co(2)-N(8)	93.1
N(2)-Co(1)-N(4)	87.1	N(7)-Co(2)-N(9)	177.6
N(2)-Co(1)-N(5)	92.0	N(7)-Co(2)-N(10)	89.8
N(3)-Co(1)-N(4)	92.7	N(8)-Co(2)-N(9)	88.2
N(3)-Co(1)-N(5)	89.8	N(8)-Co(2)-N(10)	90.1
N(4)-Co(1)-N(5)	177.3	N(9)-Co(2)-N(10)	92.2
Co(1)-O(1)-O(2)	113.2	Co(2)-O(2)-O(1)	112.3
O(3)-S(1)-O(4)	108.6	O(7)-S(2)-O(8)	112.7
O(3)-S(1)-O(5)	111.0	O(7)-S(2)-O(9)	115.8
O(3)-S(1)-O(6)	110.1	O(7)-S(2)-O(10)	105.1
O(4)-S(1)-O(5)	109.1	O(8)-S(2)-O(9)	111.7
O(4)-S(1)-O(6)	108.5	O(8)-S(2)-O(10)	106.1
O(5)-S(1)-O(6)	109.3	O(9)-S(2)-O(10)	104.4

Table VII

Rms Displacements of the Heavy Atoms along the Principal Directions of the Thermal Ellipsoids

Atom	Displacements, Å
Co(1)	0.158 (1), 0.145 (1), 0.142 (1)
O(1)	0.208 (8), 0.161 (6), 0.140 (6)
N(1)	0.198 (8), 0.188 (9), 0.158 (9)
N(2)	0.189 (9), 0.178 (7), 0.153 (7)
N(3)	0.212 (9), 0.168 (7), 0.162 (8)
N(4)	0.208 (9), 0.189 (7), 0.154 (7)
N(5)	0.173 (8), 0.172 (9), 0.156 (8)
Co(2)	0.168 (2), 0.157 (1), 0.145 (1)
O(2)	0.207 (6), 0.165 (8), 0.136 (5)
N(6)	0.200 (8), 0.196 (8), 0.172 (9)
N(7)	0.214 (9), 0.179 (7), 0.177 (9)
N(8)	0.220 (8), 0.203 (9), 0.174 (7)
N(9)	0.214 (10), 0.172 (8), 0.150 (7)
N(10)	0.229 (10), 0.187 (6), 0.163 (8)
S(1)	0.163 (3), 0.149 (2), 0.145 (2)
O(3)	0.221 (7), 0.211 (7), 0.141 (6)
O(4)	0.241 (6), 0.198 (7), 0.133 (6)
O(5)	0.222 (6), 0.203 (7), 0.149 (6)
O(6)	0.224 (6), 0.220 (7), 0.155 (6)
S(2)	0.216 (2), 0.172 (3), 0.154 (2)
O(7)	0.477 (9), 0.242 (9), 0.159 (4)
O(8)	0.241 (7), 0.229 (7), 0.178 (8)
O(9)	0.564 (12), 0.314 (9), 0.182 (6)
O(10)	0.564 (11), 0.271 (9), 0.225 (8)
O(11)	0.388 (9), 0.205 (6), 0.190 (6)
O(12)	0.305 (8), 0.264 (7), 0.188 (6)
O(13)	0.282 (7), 0.241 (6), 0.199 (7)
O(14)	0.233 (6), 0.212 (7), 0.170 (6)

B. The Sulfate Groups.—The sulfate group about S(1) is very regular. The four S–O bond lengths average 1.474 Å and the average deviation of an O–S–O angle from 109.5° is only 0.8°. The thermal motions of all of the atoms of the ion are relatively small and only moderately anisotropic (see Table VII); again, the directions of principal motion of the oxygen atoms are roughly perpendicular to the S–O bonds.

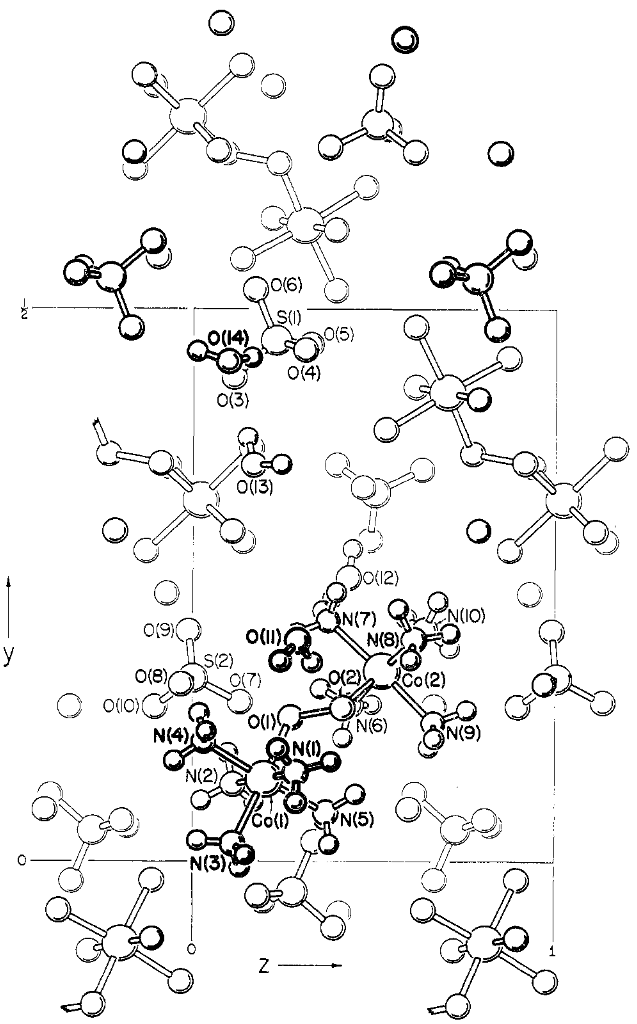

Figure 4.—A portion of the structure viewed down the *a* axis. All of the heavy atoms from $x = 0$ to $x = 1$ are shown; for clarity hydrogen atoms are shown for only one asymmetric unit.

The situation with respect to the second sulfate group is quite different. The sulfur atom S(2) has a moderately anisotropic motion, but three of the oxygen ligands—O(7), O(9), and O(10)—have thermal parameters which correspond to rms vibrations along the principal axes of as much as 0.56 Å. The calculated bond distances for these atoms (given in Table V) have to be corrected for the effects of the motion, but even when they are, the resulting sulfate group is still not regular. Correcting these distances by the formula $d_{\rm cor} = \sqrt{d^2 + (B_{\rm max}/8\pi^2)}$, they become: S(2)–O(7), 1.473 Å; S(2)–O(8), 1.483 Å; S(2)–O(9), 1.478 Å; S(2)–O(10), 1.565 Å. The angles involving the S(2)–O(10) bond are seen (Table VI) to be all smaller than tetrahedral; thus the oxygen atoms are forming a distorted tetrahedron so as to equalize the nonbonded O–O distances. The reason the S(2)–O(10) distance is long is presumably because O(10) forms a strong hydrogen bond (2.768 Å) with O(13), one of the water molecules. On the other hand, the uncertainties in these corrected bond lengths are so high that no great weight should be placed on their exact values.

The over-all thermal motion of this sulfate group can best be described as a libration of rms amplitude 20° about the S(2)–O(8) bond. The three anisotropic oxygen atoms O(7), O(9), and O(10) have their prin-

TABLE VIII

THE HYDROGEN BONDING[a]

From	To	Dist, Å	From	To	Dist, Å
N(1)	O(7), a	3.00	N(6)	O(7), a	3.16
	O(6), d	3.02		O(13), c	3.10
	O(3), c	3.23			
N(2)	O(8), a	3.07	N(7)	O(12), a	3.08
	O(6), d	3.12		O(9), c	2.91
	O(5), c	2.06		O(11), a	3.26
N(3)	O(4), c	3.07	N(8)	O(9), c	2.89
	O(5), d	3.20		O(13), c	3.01
	O(4), d	2.99			
N(4)	O(10), a	3.07	N(9)	O(3), c	3.08
	O(8), a	3.29		O(14), c	3.08
	O(4), c	3.12		[O(8), O(10)], a	3.07
N(5)	O(3), c	2.99	N(10)	O(12), a	2.98
	O(6), d	3.04		O(11), c	3.16
	O(14), d	3.10			
O(11)	O(2), a	2.82	O(13)	O(3), a	2.81
	O(7), a	2.90		O(10), c	2.77
O(12)	O(11), a	2.73	O(14)	O(4), a	2.85
	O(8), c	2.78		O(6), b	2.74

[a] The atom listed in column 1 has coordinates as given in Table III. The symmetry transformation given after the atom listed in column 2 applies to its coordinates. These transformations are: (a) x, y, z; (b) $-x, -y, -z$; (c) $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$; (d) $^1/_2 - x, ^1/_2 + y, ^1/_2 - z$, or integral unit-cell translation variants of these.

cipal axes of vibration very nearly in the plane of the circle they define and tangent to that circle.

C. The Over-all Structure.—As is shown in Figure 4, the cation is surrounded by sulfate groups and water molecules, and all of these groups are held together by an intricate network of hydrogen bonds. The hydrogen-bonding scheme is summarized in Table VIII, which lists the short N–O or C–O distances which we have interpreted as hydrogen bonds. The hydrogen atoms themselves were positioned from difference maps and in most cases their positions were unambiguous; where there was any doubt as to the placement of a hydrogen atom, the potential hydrogen bonding was considered. All but three of the ammine protons are involved in the hydrogen bonding, and all of the sulfate oxygen atoms appear to accept at least two and usually three hydrogen bonds. The water molecules each accept two hydrogen bonds from ammine groups (or water) and donate two to sulfate groups (or water). Thus the structure appears to involve a very efficient use of the available donors and acceptors, just as did the structure of the sulfate of the superoxo-bridged cation.

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Spectral Properties of Oxovanadium(IV) Complexes. I. β-Ketimines[1]

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The spectral properties of oxovanadium(IV) complexes of the β-ketimines bisacetylacetoneethylenediimine, bisbenzoylacetoneethylenediimine, bisacetylacetone-1,2-propylenediimine, and bisbenzoylacetone-1,2-propylenediimine have been studied. The visible electronic spectra, 10–25 kK, were measured with the materials in toluene, tetrahydrofuran, pyridine, chloroform, and ethanol solution. The positions of the prominent ligand field bands at ~16.4 and ~18.0 kK are nearly the same for all the complexes. Only small solvent effects are noted. These do not parallel donor strength of the solvent but appear to be more dependent on hydrogen-bonding and dielectric constant effects. Electron spin resonance spectra have been measured with the complexes in solution and in the frozen solid state. The g values, $g_0 = 1.974$, $g_{\parallel} = 1.954$, and $g_{\perp} = 1.984$, are the same for all complexes in every solvent examined. The vanadium nuclear hyperfine splittings, $A_0 = 103.8$–99.4, $A_{\parallel} = 183$–176, $A_{\perp} = 64$–61 G, vary only slightly with substituent. Solvent effects are small and can be interpreted in the same way as for the visible spectra. The electronic structure of the β-ketimine complexes is discussed by comparison to those of the β-diketone and porphyrin complexes.

Introduction

The occurrence of vanadium in petroleum is widespread.[2] Knowledge about the chemical nature of the metal atom is prerequisite to understanding not only the role that the metal plays in the origin of petroleum, but also to determine how to remove this deleterious element from petroleum products. To a very large extent the vanadium is concentrated in the solid, asphaltic fraction of petroleum[3] as oxovanadium(IV) complexes, which are classified as either porphyrin[4] or nonporphyrin. Nonporphyrin vanadium complexes have never been successfully isolated and the ligand atoms bound to the metal in these compounds are un-

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