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Structural Characterization of the $[(CN)_5CoO_2Co(CN)_5]^{6-}$ Ion: The Crystal Structure of Potassium Decacyano-μ-peroxodicobaltate Dinitrate Tetrahydrate

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The peroxo-bridged binuclear anion $[(CN)_5CoO_2 Co(CN)_5]^{6-}$ has been crystallized as a double salt with potassium nitrate in the compound $K_8[Co_2O_2 (CN)_{10}](NO_3)_2 \cdot 4H_2O$. The crystal structure of this salt has been determined using three-dimensional X-ray diffraction data measured with a computer-controlled diffractometer. Cell constants are $a = 11.605(4)$, $b = 8.383(3)$, $c = 16.639(4)$ Å, $\beta = 109.43(2)°$; the space group is $P2_1/c$, with $Z = 2$. Least-squares refinement using 2114 unique data led to an unweighted R index of 0.043. The structure consists of a quite dense packing of binuclear cobalt anions, nitrate ions, potassium ions, and water molecules, in which all water molecules are hydrogen bonded to the bridging peroxo group. The binuclear anion has point symmetry $\bar{1}$, and thus contains a planar peroxo linkage, in which the Co–O–O–Co atoms are σ-bonded in a staggered arrangement. The O–O distance has a rather short value of 1.447(4) Å. Co–C distances range from 1.874 to 1.912 Å, with the shortest trans to the bridging group. The C–N distances of the cyanide ligands range from 1.136 to 1.163 Å, averaging 1.149 Å. The Co–O distance has the extremely long value of 1.985(3) Å.

Introduction

The aqueous chemistry of the cobalt(II) cyanide system is unusual in several respects and quite complex. One of the interesting aspects of this system is that the aqueous $[Co(CN)_5]^{3-}$ ion, presumed to exist as a monomer in solution, can be very rapidly oxidized by atmospheric oxygen to form the peroxo-bridged binuclear anion $[(CN)_5CoO_2Co(CN)_5]^{6-}$, which is reasonably stable at high pH. This ion can be further oxidized by a one electron oxidation of the bridging group to the superoxo-bridged $[(CN)_5CoO_2Co(CN)_5]^{5-}$ ion. While many spectroscopic and magnetic studies have been carried out, little X-ray structural work has been reported on compounds derived from the Co(II) cyanide system, primarily due to the instability of many of the complexes and difficulty in preparing suitable crystals. Only recently has the solid-state structure of the $[Co_2(CN)_{10}]^{6-}$ dimer been reported.[1,2] Due to our interest in characterizing bonding of cobalt to dioxygen ligands, we have undertaken structural studies of the $[(CN)_5CoO_2Co(CN)_5]^{6-}$ and $[(CN)_5 CoO_2Co(CN)_5]^{5-}$ ions by single crystal X-ray diffraction techniques. Suitable single crystals containing the μ-peroxo anion have been prepared by cocrystallization of the potassium salt with KNO_3, and the structure of the double salt is reported here.

Experimental

The procedure reported by Haim and Wilmarth[3] for the preparation of the simple potassium salt $K_6[(CN)_5CoO_2Co(CN)_5] \cdot H_2O$ from $Co(NO_3)_2$ was carried out. Microscopic examination of the crude product revealed primarily thin, brown flakes which apparently lost solvent and became opaque upon drying and also a few smaller, well-formed orange crystals which remained transparent upon drying. Recrystallization by adding ethanol at 0° to a 1*M* KCN solution of this mixture yielded the transparent, orange crystals as the major product. Peroxide analysis of the orange product yielded considerably lower values than would be expected for $K_6[(CN)_5CoO_2Co(CN)_5]$ or for any conceivable hydrate of this salt. Attempts to further purify the product did not substantially affect the peroxide analysis; the UV–visible spectrum of these crystals dissolved in 1*M* aqueous KOH was identical with that reported for $K_6[(CN)_5CoO_2Co(CN)_5]$.[4] Density measurements and a preliminary survey of the reciprocal lattice by Weissenberg photography indicated a unit cell which could not contain an integral number of formulas of the simple potassium salt or any reasonable hydrate of it. Although the composition of these crystals was unknown, it was clear that they contained the desired ion and were reasonably stable; therefore they were deemed suitable for the structural study. This orange compound was subsequently demonstrated to be $K_8[Co_2O_2(CN)_{10}](NO_3)_2 \cdot 4H_2O$ by successful solution and refinement of the crystal structure.

A crystal of approximate dimensions 0.11 × 0.44 × 0.15 mm, elongated along *b*, was chosen for intensity data collection, and mounted with its *b* axis inclined about $^1/_2$ degree from the Φ axis of a locally assembled, Syntex automated E & A full-circle diffractometer. Cell dimensions were obtained from a least-squares fit of 2Θ values measured for 19 reflections, using graphite-monochromatized MoKα radiation ($\lambda = 0.71069$ Å). The density was experimentally determined by flotation in a CCl_4–$CHBr_3$ mixture. Systematic extinctions h0l with l odd and 0k0 with k odd uniquely determine the space group to be $P2_1/c$. Crystal data are given in Table I.

Intensity data were collected employing graphite-monochromatized MoKα radiation, a Θ–2Θ scan technique, and a proportional counter. Measurements were made at room temperature, and all data in one quadrant with $2\Theta < 50°$ were measured at least once. Scan widths varied linearly with 2Θ, having values of 1.9° at $2\Theta = 7°$ and 2.1° at $2\Theta = 33°$, centered on the weighted mean of the α_1 and α_2 peaks. Scan speeds also varied linearly with peak intensity between $^1/_2$ degree per minute at 10 cps and 4 degrees per minute at and above 1000 cps. Below this range, scans were made at 8 degrees per minute. Background counting times were equal at the two extremes of the scan and totaled the same as the scanning time. Four standard reflections were remeasured every 100 reflections throughout data collection, and a decrease in intensity of about 3% was noted during this time. Data were rescaled to correct for this decrease, and background, Lorentz, and polarization corrections were made. No absorption corrections were made; the linear absorption coefficient μ is 22.3 cm^{-1}, and the maximum value of μR is approximately 0.73. Observational variances for observed F values were obtained from counting statistics, including an additional term of $(0.02S)^2$ to account for uncertainty due to errors other than purely statistical uncertainty. Average F's less than 2σ above zero were set equal to zero with zero weight in subsequent calculations. Systematic absences for space group $P2_1/c$ were deleted, only 1.8% of which measured greater than 3σ above zero. Of 2806 independent reflections measured, 2114 remained to be used in the structure determination.

TABLE I. Crystal Data.

Formula:	$K_8[Co_2O_2(CN)_{10}](NO_3)_2 \cdot 4H_2O$
Formula Weight:	919.0
Space Group:	$P2_1/c$, C_{2h}^5
a:	11.605(4) Å
b:	8.383(3) Å
c:	16.639(4) Å
β:	109.43(2)°
V:	1526(1) Å^3
ϱ_o:	1.98(1) g/cm^3
ϱ_c:	2.000(2) g/cm^3
λ(MoKα)	0.71069 Å
μ(MoKα)	22.3 cm^{-1}
Habit:	{101}, {$\bar{1}$01}, {111}

Structure Solution and Refinement

A Patterson map was calculated using data with $2\Theta \leq 30°$, from which the positions of the cobalt atom and four potassium ions were deduced. This is one more potassium ion than is required for charge balance with the binuclear anion, such that another monovalent anion was sought. A Fourier synthesis phased on the heavy atoms revealed the positions of all ligand atoms, the extra anion which was identified as a nitrate ion, and the oxygen atoms of both water molecules. A structure factors calculation using all nonhydrogen atoms yielded an R value of 0.29. Thus the previously uncharacterized compound was identified as $K_8[(CN)_5CoO_2Co(CN)_5](NO_3)_2 \cdot 4H_2O$. This structure was refined by least-squares techniques. Hydrogen atoms were located by difference Fourier syntheses after partial refinement; their positions were refined, and their isotropic temperature factors were assigned values of B = 5.0 which were not refined. Machine calculations were carried out using the CRYM crystallographic computing system on an IBM 370/155 computer. Scattering factors for K^+, O, C, N, and neutral cobalt were taken from the International Tables,[5] as were $\Delta f'$ for cobalt and K^+. Hydrogen scattering factors were those of Stewart, Davidson and Simpson.[6] The quantity minimized in the least-squares calculations was $\Sigma w(F_o^2 - F_c^2)^2$, where the weights are $w = 1/\sigma^2(F_o^2)$. Refinement of the full structure utilized two matrices, one containing all positional parameters, and the other containing thermal parameters and the scale factor. The total number of parameters varied in the last cycle of least squares was 215, corresponding to a data: parameter ratio of 9.80. In this cycle, no nonhydrogen atom parameter shifted more than 30% of its esd, and no hydrogen atom parameter shifted by more than 50% of its esd. The final unweighted R index ($R = \Sigma|F_o - |F_c||/\Sigma F_o$) is 0.043, and the final "goodness of fit" ($GOF = [\Sigma w(F_o^2 - F_c^2)^2/(m-s)]^{1/2}$ is 1.77. A three dimensional difference synthesis calculated at the conclusion of the refinement indicated three peaks of density between 0.6–1.1 eÅ^{-3} in the region of the binuclear ion; however, no chemically reasonable interpretation of these peaks was apparent. The largest discrepancy between a calculated structure factor and a measured F treated as "unobserved" was slightly greater than $3\sigma(F_o)$.

TABLE II. Observed and Calculated Structure Factors. (Columns are, in order, l, $10F_{obs}$, $10F_{calc}$. An asterisk (*) after $10F_{calc}$ indicates that the reflection was not used in the refinement).

0	0	L
0	0	6969*
2	439	429
4	1444	1390
6	2504	2443
8	458	645
10	1306	1323
12	90	109
14	119	56
16	123	128
1	0	L
-16	763	742
-14	177	197
-12	773	751
-10	1017	977
-8	234	255
-6	1429	1396
-4	477	467
-2	518	508
0	379	376
2	696	733
4	753	744
6	886	859
8	1301	1321
10	927	939
12	709	746
14	551	608
16	187	218
2	0	L
-16	243	216
-14	326	321
-12	827	812
-10	76	97
-8	405	424
-6	306	277
-4	1213	1190
-2	957	907
0	390	366
2	1926	1965
4	1489	1448
6	1502	1453
8	323	313
10	675	693
12	763	771
14	664	677
16	0	0*
3	0	L
-16	252	247
-14	0	70*
-12	1257	1236
-10	82	47
-8	835	829
-6	1864	1866
-4	846	820
-2	1501	1487
0	92	7
2	822	818
4	404	418
6	113	89
8	286	278
10	535	517
12	500	477
14	198	179
16	131	155
4	0	L
-16	128	101
-14	245	252
-12	472	482
-10	141	139
-8	387	396
-6	262	233
-4	956	941
-2	1320	1295
0	270	275
2	949	942
4	72	80
6	428	421
8	0	34*
10	405	381
12	446	419
14	0	97*
5	0	L
-16	119	143
-14	561	562
-12	486	474
-10	813	778
-8	1268	1225
-6	1694	1624
-4	305	303
-2	104	100
0	1729	1729
2	522	521
4	296	303
6	157	163
8	501	502
10	425	420
12	175	172
14	144	97
6	0	L
-16	460	463
-14	532	531
-12	659	664
-10	0	33*
-8	517	495
-6	524	515
-4	834	835
-2	582	594
0	881	899
2	1149	1159
4	499	688
6	427	421
8	741	735
10	341	336
12	0	67*
7	0	L
-16	81	9
-14	111	87
-12	1015	1034
-10	215	212
-8	741	737
-6	702	697
-4	279	266
-2	784	782
0	293	288
2	117	108
4	390	383
6	0	88*
8	389	374
10	450	420
12	0	49*
8	0	L
-16	285	293
-14	248	249
-12	816	826
-10	0	35*
-8	760	748
-6	280	278
-4	402	400
-2	1209	1223
0	251	251
2	602	603
4	691	673
6	152	155
8	402	411
10	138	107
9	0	L
-16	218	192
-14	196	177
-12	200	206
-10	275	269
-8	443	447
-6	88	106
-4	305	306
-2	304	303
0	249	247
2	592	582
4	0	99*
6	0	89*
8	269	279
10	0	L
-16	135	122
-14	730	754
-12	258	255
-10	351	355
-8	216	219
-6	90	67
-4	0	6*
-2	137	137
0	320	316
2	125	141
4	285	247
6	0	10*
8	0	85*
11	0	L
-16	119	70
-14	341	329
-12	141	121
-10	442	441
-8	332	332
-6	0	91*
-4	526	529
-2	209	207
0	428	426
2	290	284
4	0	3*
6	98	123
12	0	L
-14	186	138
-12	263	260
-10	0	1*
-8	364	382
-6	0	61*
-4	147	137
-2	0	23*
0	315	303
2	146	157
0	1	L
-16	105	84
-15	84	140
-14	237	244
-13	102	156
-12	689	678
-11	281	292
-10	397	396
-9	462	470
-8	423	422
-7	293	294
-6	363	354
-5	172	178
-4	155	171
-3	1100	1063
-2	340	324
-1	495	485
1	498	485
2	340	324
3	1098	1063
4	160	171
5	166	178
6	354	354
7	259	294
8	426	422
9	450	470
10	379	396
11	274	292
12	663	678
13	100	156
14	250	244
15	94	140
16	0	84*
1	1	L
-16	0	49*
-15	266	245
-14	552	549
-13	559	533
-12	210	202
-11	224	233
-10	444	437
-9	380	375
-8	1136	1112
-7	0	60*
-6	337	339
-5	1634	1570
-4	1069	1054
-3	380	349
-2	413	392
-1	604	599
0	231	224
1	934	941
2	758	759
3	133	100
4	254	256
5	377	372
6	519	509
7	395	409
8	186	187
9	130	142
10	559	543
11	272	296
12	148	136
13	277	290
14	308	307
15	104	156
16	209	200
2	1	L
-16	298	300
-15	431	419
-14	0	78*
-13	513	501
-12	197	188
-11	373	371
-10	349	355
-9	1012	[illegible]
-8	513	499
-7	394	397
-6	1424	1410
-5	520	549
-4	729	742
-3	640	629
-2	595	563
-1	865	848
0	465	461
1	297	288
2	1056	1078
3	645	630
4	987	952
5	212	216
6	380	381
7	286	309
8	257	254
9	0	17*
10	79	44
11	141	133
12	274	275
13	188	197
14	259	260
15	107	18
16	145	70
3	1	L
-16	0	24*
-15	0	51*
-14	428	426
-13	254	272
-12	0	49*
-11	0	33*
-10	534	532
-9	508	507
-8	827	822
-7	87	103
-6	728	708
-5	1121	1105
-4	505	508
-3	277	312
-2	501	521
-1	62	46
0	381	387
1	1344	1376
2	746	731
3	447	450
4	320	308
5	241	239
6	965	938
7	554	548
8	259	261
9	374	360
10	448	464
11	211	188
12	210	212
13	262	257
14	0	0*
15	110	61
16	131	141
4	1	L
-16	413	421
-15	0	24*
-14	116	91
-13	407	408
-12	132	108
-11	76	46
-10	441	435
-9	111	84
-8	611	595
-7	800	760
-6	978	969
-5	371	371
-4	0	7*
-3	1589	1555
-2	1149	1148
-1	947	917
0	953	960
1	755	761
2	663	657
3	467	452
4	1102	1092
5	181	173
6	0	9*
7	282	281
8	870	853
9	237	224
10	0	61*
11	405	399
12	0	37*
13	209	202
14	193	169
15	0	123*
5	1	L
-16	85	114
-15	118	131
-14	0	37*
-13	171	159
-12	354	353
-11	430	426
-10	270	265
-9	455	432
-8	899	871
-7	99	100
-6	309	303
-5	358	344
-4	70	72
-3	519	512
-2	524	536
-1	124	139
0	319	331
1	858	876
2	334	288
3	473	483
4	102	83
5	217	230
6	648	639
7	614	620
8	413	416
9	123	133
10	249	237
11	155	148
12	651	638
13	122	115
14	0	72*
6	1	L
-16	334	324
-15	0	133*
-14	490	486
-13	0	90*
-12	78	22
-11	264	261
-10	753	752
-9	173	160
-8	389	388
-7	0	37*
-6	396	378
-5	69	76
-4	981	984
-3	363	399
-2	727	728
-1	0	11*
0	586	594
1	538	554
2	751	748
3	368	380
4	252	288
5	0	80*
6	661	669
7	682	663
8	0	111*
9	176	155
10	0	5*
11	298	288
12	0	66*
13	300	292
7	1	L
-16	0	70*
-15	393	412
-14	0	59*
-13	425	436
-12	562	563
-11	406	408
-10	122	56
-9	766	779
-8	1156	1150
-7	195	206
-6	310	302
-5	126	140
-4	512	522
-3	135	133
-2	392	397
-1	118	118
0	311	311
1	0	34*
2	644	652
3	168	166
4	187	177
5	215	209
6	377	365
7	0	22*
8	174	161
9	0	18*
10	0	30*
11	189	139
12	282	265
8	1	L
-16	293	295
-15	0	51*
-14	545	541
-13	346	373
-12	162	159
-11	631	642
-10	496	511
-9	349	341
-8	227	236
-7	471	453
-6	188	195
-5	767	767
-4	86	57
-3	392	405
-2	215	217
-1	565	552
0	863	872
1	415	416
2	141	137
3	254	250
4	391	376
5	89	94
6	604	583
7	0	81*
8	156	126
9	178	140
10	495	473
11	97	69
9	1	L
-16	381	378
-15	147	114
-14	138	78
-13	221	213
-12	304	516
-11	167	148
-10	910	904
-9	131	114
-8	0	50*
-7	103	65
-6	1204	1204
-5	533	532
-4	230	237
-3	0	22*
-2	507	523
-1	392	393
0	887	894
1	586	588
2	98	44
3	235	243
4	311	298
5	366	361
6	117	143
7	0	83*
8	103	10
9	166	138
10	1	L
-16	136	168
-15	217	214
-14	119	88
-13	0	64*
-12	0	116*
-11	610	618
-10	0	90*
-9	0	10*
-8	233	249
-7	130	149
-6	0	55*
-5	460	467
-4	111	39
-3	0	110*
-2	230	239
-1	372	374
0	510	537
1	271	271
2	257	245
3	144	147
4	300	286
5	166	145
6	400	373
7	0	73*
11	1	L
-16	124	106
-15	121	1
-14	0	68*
-13	141	99
-12	0	14*
-11	0	83*
-10	128	149
-9	164	136
-8	0	42*
-7	220	223
-6	125	98
-5	78	15
-4	494	489
-3	231	223
-2	310	301
-1	220	194
0	244	247
1	309	313
2	202	206
3	265	242
4	372	349
5	124	73
12	1	L
-14	280	292
-13	0	19*
-12	559	556
-11	86	5
-10	124	147
-9	169	158
-8	432	424
-7	274	276
-6	0	60*
-5	0	83*
-4	0	33*
-3	0	58*
-2	172	163
-1	134	127
0	0	47*
1	701	166
2	0	115*
3	113	117
0	2	L
-16	162	156
-15	408	385
-14	316	291
-13	122	112
-12	0	89*
-11	1020	1018
-10	374	356
-9	253	247
-8	0	82*
-7	744	757
-6	0	38*
-5	1130	1110
-4	636	630
-3	124	114
-2	43	62
-1	802	775
0	956	970
1	787	775
2	0	62*
3	132	114
4	636	630
5	1155	1110
6	92	38
7	758	737
8	89	82
9	246	247
10	356	356
11	997	1018
12	128	89
13	0	112*
14	296	291
15	368	385
16	127	156
1	2	L
-16	337	349
-15	361	348
-14	432	416
-13	92	6
-12	0	6*
-11	631	677
-10	206	219
-9	369	372
-8	0	13*
-7	505	501
-6	1031	998
-5	1844	1830
-4	558	512
-3	385	357
-2	187	186
-1	987	978
0	40	20
1	1718	1758
2	672	636
3	1085	1040
4	179	168
5	1192	1201
6	241	227
7	537	560
8	0	75*
9	176	154
10	184	163
11	298	312
12	0	73*
13	0	21*
14	112	57
15	336	339
16	0	25*
2	2	L
-16	0	48*
-15	261	255
-14	224	218
-13	396	352
-12	192	221
-11	0	11*
-10	394	387
-9	216	207
-8	68	25
-7	993	986
-6	219	189
-5	625	616
-4	219	231
-3	179	170
-2	0	11*
-1	1039	1044
0	218	229
1	410	435
2	1060	1066
3	1924	1930
4	205	198
5	513	513
6	518	524
7	361	371
8	239	242
9	1232	1221
10	205	185
11	537	535
12	316	347
13	482	511
14	232	215
15	212	238
16	0	49*
3	2	L
-16	90	131
-15	150	151
-14	118	102
-13	553	558
-12	626	625
-11	503	514
-10	587	583
-9	582	585
-8	0	51*
-7	344	348
-6	337	330
-5	286	278
-4	1127	1116
-3	198	191
-2	1502	1477
-1	0	72*
0	407	413
1	723	712
2	320	319
3	56	76
4	390	400
5	87	41
6	416	395
7	363	352
8	134	139
9	363	373
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12	200	191
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7	175	172
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3	0	68*
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7	0	73*
8	86	7
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11	202	159
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13	212	163
14	0	83*
15	376	357
2	5	L
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-15	213	198
-14	284	289
-13	273	285
-12	229	214
-11	523	532
-10	320	336
-9	220	222
-8	0	72*
-7	898	882
-6	380	376
-5	208	209
-4	781	766
-3	323	314
-2	321	319
-1	489	494
0	464	475
1	0	31*
2	718	728
3	290	299
4	155	150
5	86	75
6	316	318
7	271	281
8	443	447
9	0	9*
10	144	159
11	125	86
12	145	145
13	253	256
14	250	257
3	5	L
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-15	182	163
-14	477	489
-13	148	140
-12	167	158
-11	130	113
-10	116	81
-9	87	89
-8	768	767
-7	588	594
-6	163	159
-5	465	451
-4	500	486
-3	696	684
-2	672	669
-1	393	391
0	284	295
1	640	694
2	225	232
3	471	482
4	117	98
5	324	334
6	613	614
7	747	761
8	149	113
9	0	35*
10	179	192
11	297	284
12	237	245
13	0	83*
14	117	64
4	5	L
-16	165	141
-15	491	478
-14	0	60*
-13	203	190
-12	117	58
-11	296	307
-10	286	276
-9	590	591
-8	0	25*
-7	393	385
-6	202	207
-5	802	795
-4	808	809
-3	659	655
-2	153	147
-1	486	499
0	502	522
1	76	59
2	723	743
3	627	650
4	273	271
5	155	136
6	574	591
7	380	381
8	414	411
9	312	328
10	0	72*
11	203	217
12	94	125
13	255	261
5	5	L
-16	0	27*
-15	114	91
-14	227	236
-13	481	459
-12	0	16*
-11	0	22*
-10	135	101
-9	491	485
-8	300	306
-7	534	534
-6	106	80
-5	479	488
-4	0	41*
-3	356	355
-2	643	640
-1	374	374
0	0	14*
1	131	137
2	168	176
3	279	280
4	0	40*
5	329	341
6	552	555
7	0	60*
8	227	224
9	115	111
10	0	56*
11	163	133
12	405	383
6	5	L
-16	327	329
-15	0	99*
-14	286	285
-13	0	104*
-12	142	134
-11	0	76*
-10	220	219
-9	234	233
-8	173	172
-7	169	184
-6	133	126
-5	570	565
-4	380	387
-3	0	16*
-2	170	160
-1	436	443
0	0	68*
1	68	80
2	346	353
3	181	196
4	0	66*
5	544	549
6	182	198
7	0	16*
8	400	403
9	209	214
10	0	55*
11	0	21*
7	5	L
-16	157	174
-15	0	43*
-14	0	54*
-13	0	65*
-12	240	248
-11	286	292
-10	375	361
-9	451	448
-8	100	82
-7	281	296
-6	556	554
-5	166	143
-4	331	325
-3	170	167
-2	0	21*
-1	0	119*
0	324	332
1	0	6*
2	131	139
3	121	140
4	0	7*
5	251	242
6	263	275
7	125	138
8	125	116
9	0	78*
8	5	L
-15	216	218
-14	263	255
-13	299	300
-12	151	142
-11	192	180
-10	263	271
-9	116	123
-8	0	22*
-7	366	375
-6	0	13*
-5	156	138
-4	0	29*
-3	312	328
-2	362	363
-1	0	1*
0	362	363
1	195	209
2	241	246
3	196	193
4	227	215
5	0	42*
6	223	209
7	272	256
8	0	53*
9	5	L
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-13	76	57
-12	329	328
-11	0	1*
-10	339	339
-9	0	75*
-8	196	190
-7	357	349
-6	524	522
-5	244	243
-4	495	501
-3	247	259
-2	142	121
-1	95	18
0	308	306
1	0	12*
2	144	139
3	457	460
4	0	75*
5	0	46*
6	117	112
10	5	L
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-12	99	142
-11	0	6*
-10	150	134
-9	399	385
-8	0	7*
-7	271	273
-6	298	314
-5	298	282
-4	102	110
-3	319	318
-2	284	284
-1	95	111
0	336	329
1	106	63
2	151	152
3	89	78
4	351	344
11	5	L
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-10	165	122
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-7	88	21
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-5	291	287
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-2	0	1*
-1	374	359
0	240	226
1	148	165
0	6	L
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-13	562	554
-12	98	58
-11	103	100
-10	119	117
-9	552	540
-8	260	245
-7	0	38*
-6	344	345
-5	388	375
-4	96	100
-3	600	564
-2	0	9*
-1	423	411
0	662	675
1	612	611
2	0	9*
3	575	564
4	114	100
5	374	375
6	335	345
7	86	38
8	246	245
9	529	540
10	147	117
11	120	100
12	84	58
13	533	554
14	213	197
1	6	L
-15	128	20
-14	135	107
-13	444	460
-12	124	61
-11	85	73
-10	141	122
-9	0	8*
-8	246	252
-7	657	650
-6	0	23*
-5	545	550
-4	299	295
-3	618	595
-2	0	76*
-1	475	463
0	0	3*
1	783	799
2	93	80
3	393	375
4	461	462
5	475	471
6	0	83*
7	293	313
8	0	48*
9	0	69*
10	253	261
11	197	203
12	0	46*
13	0	32*
14	0	12*
2	6	L
-15	174	110
-14	0	82*
-13	0	100*
-12	0	57*
-11	123	71
-10	0	91*
-9	142	130
-8	299	298
-7	0	46*
-6	0	60*
-5	278	264
-4	185	175
-3	0	68*
-2	292	293
-1	0	105*
0	207	209
1	680	696
2	59	46
3	315	324
4	257	260
5	426	436
6	197	196
7	207	207
8	0	11*
9	159	186
10	176	121
11	721	735
12	0	1*
13	0	57*
3	6	L
-15	343	342
-14	115	111
-13	0	22*
-12	269	256
-11	405	374
-10	0	50*
-9	100	70
-8	545	539
-7	267	276
-6	311	309
-5	480	481
-4	338	334
-3	431	414
-2	137	141
-1	507	509
0	147	135
1	78	57
2	265	277
3	0	57*
4	0	27*
5	102	129
6	89	82
7	96	120
8	0	13*
9	0	60*
10	127	127
11	138	144
12	0	2*
4	6	L
-15	305	299
-14	0	8*
-13	258	253
-12	167	149
-11	312	307
-10	0	31*
-9	391	370
-8	348	346
-7	536	547
-6	166	130
-5	514	516
-4	83	31
-3	453	490
-2	322	319
-1	511	530
0	63	62
1	143	148
2	109	119
3	262	264
4	281	279
5	180	177
6	197	189
7	568	567
8	101	82
9	138	148
10	0	21*
11	135	69
5	6	L
-15	0	3*
-14	0	92*
-13	396	409
-12	195	165
-11	0	71*
-10	97	96
-9	199	183
-8	0	99*
-7	0	19*
-6	401	393
-5	116	109
-4	190	177
-3	0	17*
-2	221	234
-1	495	512
0	152	200
1	122	137
2	419	492
3	488	489
4	0	120*
5	399	415
6	0	5*
7	312	322
8	117	113
9	456	439
10	202	179
6	6	L
-15	0	52*
-14	0	129*
-13	670	665
-12	394	379
-11	259	269
-10	146	187
-9	324	324
-8	167	157
-7	840	825
-6	387	381
-5	416	416
-4	0	43*
-3	519	509
-2	0	29*
-1	257	253
0	102	103
1	205	210
2	161	168
3	172	158
4	107	150
5	229	230
6	0	24*
7	87	21
8	0	21*
9	0	88*
7	6	L
-14	110	100
-13	149	144
-12	0	20*
-11	0	98*
-10	165	178
-9	332	321
-8	90	74
-7	262	250
-6	111	120
-5	254	248
-4	77	66
-3	489	495
-2	0	43*
-1	83	126
0	96	113
1	594	600
2	0	81*
3	407	402
4	155	131
5	555	546
6	132	83
7	274	289
8	0	41*
8	6	L
-14	112	113
-13	95	82
-12	0	9*
-11	340	332
-10	266	255
-9	102	57
-8	149	127
-7	235	242
-6	138	93
-5	202	206
-4	391	395
-3	346	347
-2	107	111
-1	234	229
0	203	215
1	252	241
2	0	85*
3	165	176
4	165	142
5	119	112
6	236	161
9	6	L
-12	119	88
-11	375	369
-10	274	273
-9	239	234
-8	227	208
-7	314	309
-6	0	59*
-5	239	241
-4	225	206
-3	119	106
-2	112	74
-1	404	417
0	147	109
1	166	155
2	68	92
3	247	232
4	91	94
10	6	L
-11	286	279
-10	0	6*
-9	0	126*
-8	0	51*
-7	266	248
-6	164	182
-5	278	272
-4	0	110*
-3	207	215
-2	0	32*
-1	422	411
0	0	51*
1	75	73
11	6	L
-5	0	50*
0	7	L
-13	150	176
-12	0	25*
-11	0	8*
-10	484	463
-9	542	526
-8	203	211
-7	0	1*
-6	81	94
-5	106	117
-4	264	257
-3	405	384
-2	0	0*
-1	242	243
1	246	243
2	0	0*
3	396	384
4	261	257
5	132	117
6	113	54
7	0	1*
8	201	211
9	519	526
10	461	463
11	0	8*
12	0	25*
13	192	176
1	7	L
-13	277	294
-12	303	298
-11	128	75
-10	286	276
-9	146	176
-8	109	106
-7	181	169
-6	561	561
-5	439	419
-4	223	205
-3	0	45*
-2	535	518
-1	221	208
0	530	549
1	458	473
2	204	199
3	127	124
4	490	488
5	241	244
6	155	123
7	90	11
8	0	72*
9	182	185
10	118	84
11	0	34*
12	0	101*
2	7	L
-13	271	257
-12	0	27*
-11	304	294
-10	284	255
-9	238	238
-8	0	70*
-7	531	522
-6	304	297
-5	0	39*
-4	226	221
-3	611	603
-2	297	278
-1	143	131
0	492	505
1	226	219
2	98	89
3	117	135
4	315	296
5	387	400
6	346	344
7	0	33*
8	279	279
9	100	42
10	374	373
11	162	170
12	253	245
3	7	L
-14	168	139
-13	117	148
-12	252	236
-11	116	114
-10	241	233
-9	90	126
-8	180	189
-7	245	245
-6	195	195
-5	317	299
-4	185	176
-3	544	534
-2	180	184
-1	247	247
0	225	244
1	441	446
2	133	133
3	412	417
4	0	44*
5	0	41*
6	129	68
7	439	450
8	373	398
9	102	115
10	0	6*
11	47	116
4	7	L
-14	96	107
-13	109	67
-12	326	326
-11	0	39*
-10	0	75*
-9	361	362
-8	365	350
-7	0	43*
-6	138	160
-5	348	339
-4	360	366
-3	111	129
-2	267	271
-1	151	153
0	64	62
1	64	107
2	186	196
3	144	113
4	0	59*
5	0	35*
6	197	153
7	413	410
8	88	46
9	0	23*
10	175	201
5	7	L
-13	0	4*
-12	87	74
-11	0	20*
-10	181	107
-9	488	469
-8	0	2*
-7	163	125
-6	0	33*
-5	353	356
-4	277	286
-3	279	269
-2	87	160
-1	0	20*
0	0	63*
1	439	454
2	264	276
3	260	242
4	243	238
5	190	191
6	153	152
7	287	282
8	119	130
9	201	209
6	7	L
-13	0	32*
-12	290	294
-11	127	141
-10	132	153
-9	0	35*
-8	229	224
-7	0	92*
-6	441	439
-5	319	316
-4	98	66
-3	295	284
-2	304	296
-1	222	228
0	71	61
1	91	62
2	161	174
3	0	41*
4	188	180
5	355	345
6	126	130
7	85	35
7	7	L
-12	95	135
-11	383	381
-10	263	242
-9	0	48*
-8	112	100
-7	149	108
-6	223	177
-5	174	174
-4	178	190
-3	0	73*
-2	282	284
-1	106	99
0	324	318
1	118	129
2	317	310
3	93	81
4	327	314
5	310	302
8	7	L
-11	428	415
-10	114	30
-9	279	273
-8	0	92*
-7	316	323
-6	202	185
-5	380	395
-4	0	40*
-3	213	207
-2	105	139
-1	186	109
0	0	20*
1	348	347
2	171	154
3	0	3*
9	7	L
-9	240	229
-8	291	278
-7	442	428
-6	113	44
-5	0	89*
-4	166	157
-3	113	70
-2	137	158
-1	298	293
0	0	23*
0	8	L
-11	0	50*
-10	137	146
-9	131	131
-8	439	416
-7	223	201
-6	183	180
-5	219	209
-4	238	226
-3	350	348
-2	676	643
-1	294	275
0	277	277
1	275	273
2	653	643
3	359	348
4	222	226
5	213	209
6	172	180
7	208	201
8	421	418
9	146	131
10	159	146
11	0	50*
1	8	L
-11	90	24
-10	286	278
-9	239	201
-8	99	126
-7	0	20*
-6	0	27*
-5	0	99*
-4	98	59
-3	0	66*
-2	247	234
-1	0	117*
0	70	43
1	95	102
2	209	214
3	179	192
4	116	148
5	125	140
6	212	207
7	152	157
8	323	323
9	0	5*
10	302	312
2	8	L
-11	0	103*
-10	409	390
-9	0	71*
-8	220	219
-7	0	32*
-6	237	225
-5	293	287
-4	290	283
-3	102	77
-2	383	364
-1	0	52*
0	377	380
1	0	0*
2	0	41*
3	145	145
4	367	362
5	224	221
6	85	15
7	0	85*
8	0	54*
9	0	6*
3	8	L
-11	261	249
-10	246	235
-9	219	173
-8	0	90*
-7	181	169
-6	0	6*
-5	281	252
-4	368	349
-3	352	351
-2	0	20*
-1	0	13*
0	295	305
1	0	16*
2	204	209
3	118	135
4	263	257
5	213	175
6	223	214
7	204	160
8	111	102
4	8	L
-11	0	55*
-10	157	130
-9	0	93*
-8	80	39
-7	344	332
-6	0	71*
-5	106	13
-4	144	84
-3	0	83*
-2	0	22*
-1	241	245
0	0	5*
1	269	280
2	0	35*
3	0	76*
4	137	195
5	0	29*
6	0	38*
7	0	121*
5	8	L
-11	147	151
-10	258	228
-9	0	63*
-8	494	460
-7	86	113
-6	229	211
-5	0	44*
-4	119	92
-3	111	109
-2	485	472
-1	258	255
0	127	104
1	197	184
2	388	394
3	223	236
4	104	132
5	90	43
6	0	49*
6	8	L
-10	0	72*
-9	118	21
-8	0	42*
-7	138	122
-6	262	248
-5	122	83
-4	139	150
-3	94	9
-2	382	379
-1	122	125
0	376	389
1	0	53*
2	377	392
3	131	150
4	309	300
7	8	L
-9	0	91*
-8	335	324
-7	0	20*
-6	226	206
-5	214	205
-4	254	254
-3	93	60
-2	129	121
-1	140	90
0	181	200
1	0	6*
2	144	113
8	8	L
-6	217	159
-5	0	23*
-4	475	450
-3	0	6*
-2	277	269

Results and Discussion

This structure is composed of discrete potassium ions, binuclear anions of charge (–6), nitrate anions, and neutral water molecules, packed efficiently into a quite dense arrangement. Positional and thermal parameters obtained for all atoms in the structure are presented in Table III.

The Binuclear Anion

The $[(CN)_5CoO_2Co(CN)_5]^{6-}$ anion, the geometry of which is of primary interest in this investigation, is found to contain a planar CoOOCo linkage with the dioxygen group in the same sort of staggered configuration seen in the μ-peroxodicobalt decaamines.[7,8,9] Bonding distances in this ion are illustrated in Figure 1, and important angles are given in Table IV.

The Co–O distance determined in this structure, 1.985(3) Å, is quite long, and is the subject of some surprise. The distance found in singly-bridged μ-dioxygen dicobalt complexes with nitrogen donor ligands is reasonably constant with an average value (5 structures) of 1.889(7) Å, which is almost 0.1 Å shorter than the present value (see Table V). This is a very large, highly significant difference, which may be due in part to the distortions imposed upon the ion by water molecules hydrogen bonded to the bridging group, as will be discussed later. Evidence that this long Co–O distance may be caused by electronic effects is seen in the Co–C distances. The average value of the equatorial Co–C distances is 1.900(4) Å, which agrees well with the value of 1.890 Å observed in cobalt pentacyanides and hexacyanides (average of 9 structures, see Table V). The *trans* distance, however, is 1.875(4) Å, almost 4σ shorter than the equatorial average; this difference is considered significant. That a long Co–O distance is associated with a short Co–C distance *trans* to the bridging group is suggestive of electronic effects. This shortening is in sharp contrast to the *trans*-lengthening which has been observed in

TABLE III. Positional and Thermal Parameters.[a,b,c,d]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	81870(4)	12434(5)	1256(3)	184(2)	177(2)	183(3)	11(2)	93(2)	2(2)
K(1)	34325(8)	14834(12)	46478(7)	327(5)	606(7)	663(7)	36(4)	172(5)	–280(6)
K(2)	60061(8)	19597(12)	19228(6)	329(5)	654(6)	365(6)	47(5)	106(4)	62(5)
K(3)	182(8)	20309(10)	28758(6)	386(5)	348(5)	315(5)	–24(4)	180(4)	–3(4)
K(4)	23515(7)	34397(9)	17297(6)	368(5)	335(5)	345(5)	1(4)	172(4)	–64(4)
O(1)	96233(22)	–1493(32)	2620(19)	398(16)	379(16)	609(21)	60(13)	354(15)	69(15)
C(1)	68013(30)	23998(40)	1199(22)	285(19)	268(20)	219(21)	21(17)	129(17)	–1(16)
N(1)	59570(29)	30809(41)	1457(22)	391(19)	501(21)	416(23)	151(17)	199(18)	42(18)
C(2)	91572(30)	28795(40)	8352(22)	252(18)	241(21)	241(21)	19(16)	81(17)	71(17)
N(2)	96767(28)	38967(35)	12678(21)	404(19)	267(18)	398(21)	–50(15)	49(17)	–15(16)
C(3)	71073(30)	–2723(38)	–5907(21)	291(19)	207(19)	200(21)	35(15)	118(17)	34(16)
N(3)	64249(28)	–11697(36)	–9938(21)	401(19)	333(18)	353(20)	–11(15)	101(16)	–65(17)
C(4)	80897(28)	1554(38)	10959(23)	214(18)	185(19)	273(22)	12(14)	77(17)	–4(16)
N(4)	79843(27)	–5010(37)	16833(20)	375(19)	370(19)	317(20)	4(16)	137(16)	34(17)
C(5)	81683(27)	23996(38)	–8574(22)	177(17)	206(19)	268(21)	–20(14)	93(16)	–42(17)
N(5)	80888(28)	31091(36)	–14652(20)	396(18)	348(18)	328(21)	–13(15)	189(16)	85(17)
N(6)	44787(31)	7957(44)	30990(21)	437(21)	640(26)	282(20)	45(19)	152(17)	0(19)
O(2)	45540(30)	22437(37)	29864(20)	785(23)	507(21)	502(21)	139(17)	227(19)	84(17)
O(3)	53605(25)	–989(38)	31687(23)	422(18)	536(20)	1035(31)	130(15)	320(19)	–51(20)
O(4)	35005(26)	2164(43)	31404(20)	400(17)	1025(26)	492(21)	–8(18)	232(16)	14(20)
O(5)	12264(25)	18507(34)	48235(21)	335(14)	275(15)	598(21)	–38(13)	196(14)	–62(14)
O(6)	10887(25)	4526(37)	19111(19)	376(16)	557(18)	316(18)	176(15)	89(14)	–38(15)

	x	*y*	*z*	*B*
H(1)	717(42)	1248(53)	4752(29)	5.0
H(2)	926(40)	2624(53)	4859(29)	5.0
H(3)	731(37)	344(49)	1345(28)	5.0
H(4)	1741(39)	30(51)	2068(29)	5.0

[a] All coordinates have been multiplied by 10^5. [b] Temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. [c] All U's have been multiplied by 10^4. [d] Estimated standard deviations are given in parentheses.

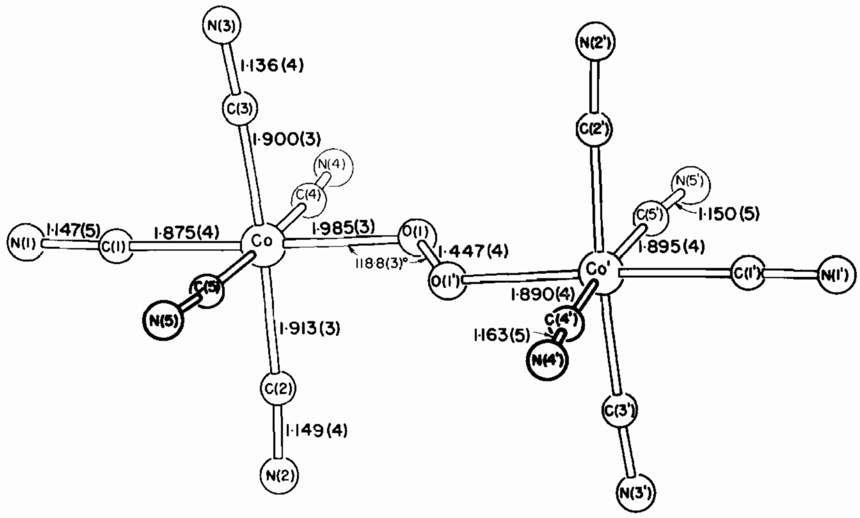

Figure 1. Interatomic distances within the $[(CN)_5CoO_2Co(CN)_5]^{6-}$ anion. Esd's are given in parentheses.

TABLE IV. Angles in the Binuclear Anion.

Atoms	Angle (Degrees)	Atoms	Angle (Degrees)
Co–C(1)–N(1)	177.4(4)	O(1)–Co–C(2)	93.0(1)
Co–C(2)–N(2)	175.9(3)	O(1)–Co–C(3)	91.8(1)
Co–C(3)–N(3)	176.5(4)	O(1)–Co–C(4)	84.5(2)
Co–C(4)–N(4)	177.5(4)	O(1)–Co–C(5)	99.6(2)
Co–C(5)–N(5)	176.3(3)		
C(1)–Co–O(1)	172.2(2)	C(2)–Co–C(3)	175.2(2)
C(1)–Co–C(2)	87.7(2)	C(2)–Co–C(4)	90.5(2)
C(1)–Co–C(3)	87.6(2)	C(2)–Co–C(5)	90.1(2)
C(1)–Co–C(4)	87.7(2)	C(3)–Co–C(4)	89.9(2)
C(1)–Co–C(5)	88.1(2)	C(3)–Co–C(5)	89.1(2)
		C(4)–Co–C(5)	175.7(2)

Geometry of the nitrate ion

Atoms	Distance or Angle
N(6)–O(2)	1.236(5) Å
N(6)–O(3)	1.243(5)
N(6)–O(4)	1.258(5)
O(2)–N(6)–O(3)	120.6(4)°
O(2)–N(6)–O(4)	119.9(4)
O(3)–N(6)–O(4)	119.5(4)

μ-peroxodicobalt amines,[7,9] and closely resembles the effect observed upon the *trans* Co–C distance caused by N-bonded cyanide in $(NH_3)_5CoCNCo(CN)_5$.[10]

The O–O distance of 1.447(4) Å is slightly shorter than the 1.471 Å found in the analogous decaammine complex,[7,8] but is sufficiently longer than the distance of about 1.31 Å expected for a superoxo bridge such that it may be definitely described as a peroxide. The most precise determination of the solid phase structure of H_2O_2, a neutron diffraction study,[11] places the O–O distance at 1.453(7) Å, in excellent agreement with the value found here. It appears that there may be a correlation between Co–O and O–O distances in peroxo-bridged dicobalt complexes. The dicobalt ammines appear to have O–O distances slightly longer than that found in H_2O_2 and short Co–O distances, while this complex has weaker bonding between the cobalt atom and the bridging group, resulting in an O–O distance which looks more like that in hydrogen peroxide. Since this is the first structure reported for a μ-O_2^{2-} cyanide, and there appear to be several possible causes for the Co–O lengthening, more structural data must be awaited to determine if the correlation is real.

The C–N distances of the cyanide ligands range from 1.136 Å to 1.163 Å and average 1.149(6) Å. This distance is very nearly the value of the average C–N distance found in binuclear cobalt cyanides and mononuclear cobalt hexacyanides, 1.147 Å (9 structures, see Table V). The Co–Co distance, always a subject of interest in binuclear structures, is 4.899(2) Å.

Examination of Figures 1 and 2 and of the angles given in Table IV makes it clear that the equatorial cyanide ligands are bent outward from the central portion of the ion. The cobalt atom lies about 0.07 Å out of the best plane of the four equatorial carbon atoms and about 0.20 Å out of the best plane of the four equatorial nitrogen atoms. Deviations from these planes of the atoms comprising the planes are about 0.005 Å and 0.01 Å, respectively. The obvious cause for this outward bending is the four water molecules hydrogen bonded to the bridging group. Figure 2 illustrates that these water molecules complete a roughly tetrahedral coordi-

TABLE V. Summary of Geometries of Related Complexes.

μ-dioxygen Dicobalt Complexes:

Compound	Co–O	O–O	O–O Torsion	Average Equatorial Co–N	Average Axial Co–N	Ref.
$[Co_2O_2(NH_3)_{10}](SO_4)_2 \cdot 4H_2O$	1.882 Å	1.473 Å	146°	1.957	1.983	7
$[Co_2O_2(NH_3)_{10}](SCN)_4$	1.879	1.469	180	1.955	1.971	8
$[Co_2O_2(en)_2(dien)_2](ClO_4)_4$	1.896	1.488	180	1.952	1.998	9
$K_8[Co_2O_2(CN)_{10}](NO_3)_2 \cdot 4H_2O$	1.985	1.447	180	–	–	This work
$[Co_2O_2(NH_3)_{10}](SO_4)(HSO_4)_3$	1.894	1.312	175	1.943	1.958	12
$[Co_2O_2(NH_3)_{10}](NO_3)_5$	1.895	1.317	180	1.957	1.955	13

Binuclear Cobalt Cyanides and Cobalt Hexacyanides:

Compound	Average Equatorial Co–C	Average C–N	Reference
$(NH_3)_3CoNCCo(CN)_5 \cdot H_2O$	1.893 Å	1.144 Å	14
$(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$	1.908	1.125	11
$(NH_3)_5CoNCSCo(CN)_5 \cdot H_2O$	1.884	1.143	15
$Ba_3[Co_2(CN)_{10}] \cdot 13H_2O$	1.885	1.153	1,2
$D_3[Co(CN)_6]$	1.883	1.147	16
$Cd_3[Co(CN)_6]_2$	1.893	1.151	17
$H_3[Co(CN)_6]$	1.885	1.154	18
$[Co(NH_3)_6][Co(CN)_6]$	1.894	1.157	19
$Cs_2Li[Co(CN)_6]$	1.886	1.148	20
Averages:	1.890 Å	1.147 Å	

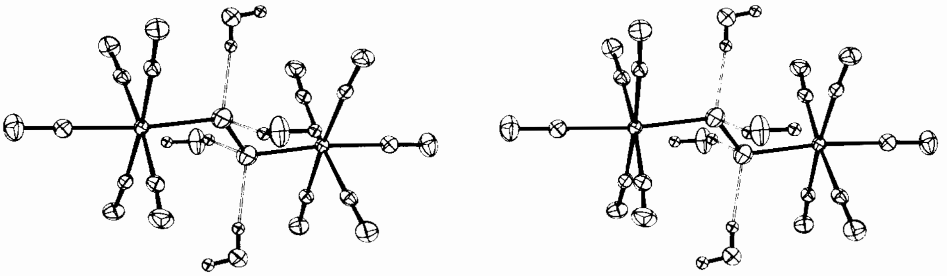

Figure 2. ORTEP stereopair illustrating the binuclear anion and hydrogen bonding to it. Thermal ellipsoids are drawn at the 40% probability level.

nation for each of the peroxy oxygen atoms, and Figure 3 indicates the manner in which these molecules lie staggered between the equatorial cyanide ligands. These hydrogen bonds are strong. The hydrogen bond involving O(5) has an O···O distance of 2.69 Å, an H···O distance of 1.95 Å, and an O–H···O angle of 165°. The hydrogen bond involving O(6) has an O···O distance of 2.75 Å, an H···O distance of 1.83 Å, and an O–H···O angle of 165°. Hydrogen bonding to the bridging group of this highly charged ion by water molecules is apparently quite favorable, as it presumably removes negative charge from the ion even at the expense of water–cyanide repulsion.

The abnormally long Co–O bond, which is certainly caused at least in part by distortions due to the water, is further evidence of the desirability of hydrogen bonding. Although hydrogen bonding to the bridging group has been observed before, all previous examples have involved intraionic bonds from ammine or substituted ammine ligands of the same ion.[9,12] The less bulky cyanide ligands apparently shield the bridging peroxide more poorly than do ammines, and allow the approach of water molecules with a small amount of distortion of the binuclear ion.

That there exist only these four hydrogen bonds, and no others, to this anion which contains a planar Co–O–O–Co linkage, strengthens our ideas about hydrogen bonding and the planarity of peroxides. As was the case in the structures of $[(en)(dien)CoO_2Co(en)(dien)](ClO_4)_4$ and $[(NH_3)_5CoO_2Co(NH_3)_5]$

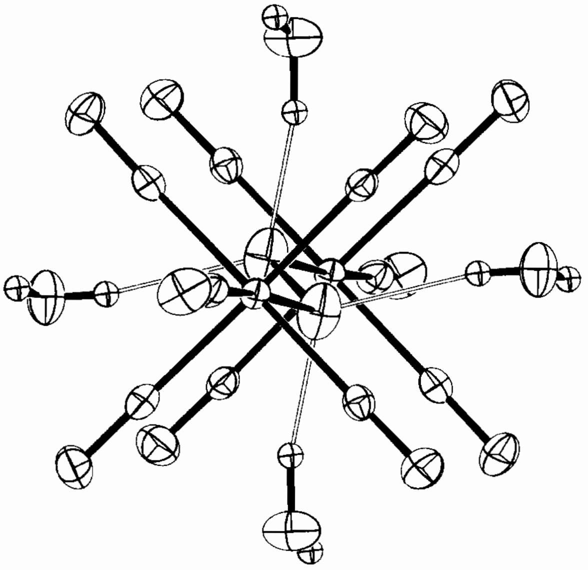

Figure 3. An ORTEP drawing of the binuclear anion illustrating the eclipsed conformation of the equatorial ligands and the staggering of the water molecules between them. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are represented by spheres of arbitrary radius.

$(SCN)_4$, there exists here a highly charged ion without an extensive system of hydrogen bonding to distribute this charge away from the cobalt centers, and the resulting Coulombic repulsion forces the ion to be planar.

Comparison of this structure with that of the corresponding μ-peroxo decaammine compound reveals the result of "replacing" the ammine ligands with cyanides. Although the details of the two ions are different, they are qualitatively the same; in each the two cobalt atoms are identical, the bridging ligand is a peroxide, and it is arranged in a σ-bonded configuration rather than the π-bonded perpendicular arrangement.

The Nitrate Ion

The nitrate ion and its surroundings are shown in Figure 4; distances and angles within the ion are given in Table 4. Within the precision of this experiment, the ion is perfectly planar and the oxygen atoms form a perfect equilateral triangle, the nonbonded O–O distance in the triangle being 2.157(3) Å. The nitrogen atom is slightly removed within the plane from the center of the triangle, causing the N–O(4) distance to be longer than the two other N–O distances by an amount of borderline statistical significance. It is perhaps worthy of note that O(4) differs from the other two oxygen atoms in being hydrogen bonded to a water molecule [O(6)] rather than having a close contact to another NO_3^- ion. This hydrogen bond is rather strong, with an O· · ·O distance of 2.87 Å, an H· · ·O distance of 2.22 Å, and an O–H· · ·O angle of 137°. The apparent thermal amplitudes of the atoms of the nitrate ion, while the largest in the structure, are of reasonable magnitude and orientation to be interpreted as real thermal vibrations of an ordered group. This thermal motion is primarily of a rotational nature around the pseudo-threefold axis of the ion, as shown in Figure 4.

The Potassium Ions

The four independent potassium ions of the structure have irregular coordination spheres, and any attempt to classify them as distorted forms of idealized polyhedra would be pointless. Closest contacts to the K^+ ions are listed in Table VI. These ions are aniso-

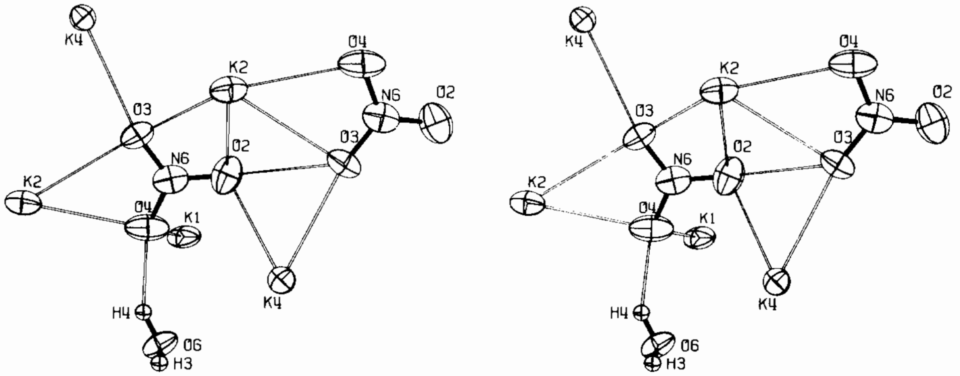

Figure 4. The nitrate ion and its surroundings. The two nitrate ions shown are related by a 2_1 axis at $^1/_2$, y, $^1/_4$, and the length of the interionic contact O(2)· · ·O(3) is 2.97 Å. Other contacts are listed in Table VI or the text. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are represented by spheres of arbitrary radius.

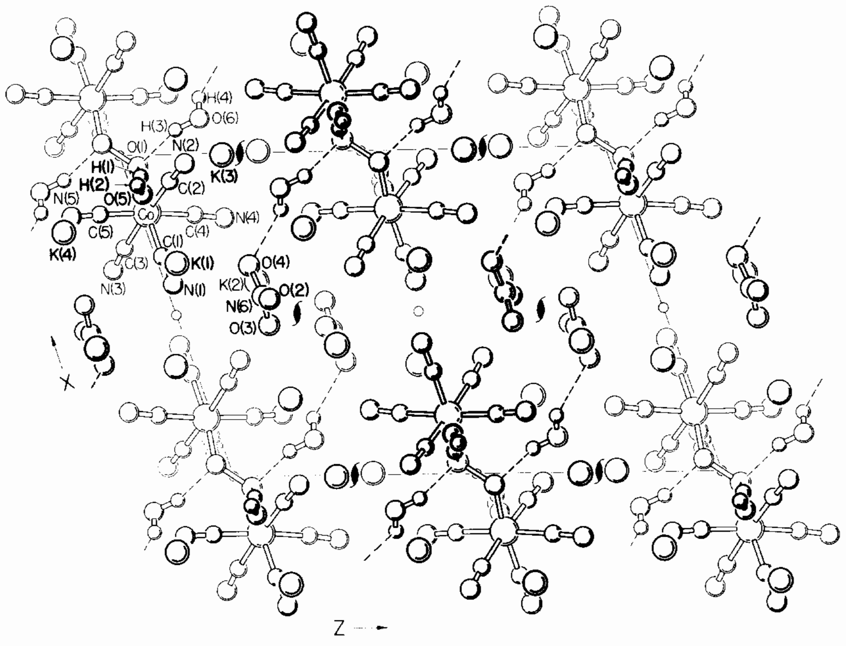

Figure 5. The crystal packing, viewed in projection down the *b* axis.

TABLE VI. Closest Contacts (Less than 3.3 Å) to the Potassium Ions.

Contact	Distance (Å)	Contact	Distance (Å)
K(1)· · ·O(4)	2.75	K(3)· · ·O(5)	3.08
K(1)· · ·O(5)	2.69	K(3)· · ·O(6)	2.68
K(1)· · ·N(1)	2.79	K(3)· · ·O(6′)	3.21
K(1)· · ·N(1′)	2.93	K(3)· · ·N(2)	2.95
		K(3)· · ·N(2′)	3.01
K(2)· · ·O(2)	2.83	K(3)· · ·N(4)	3.01
K(2)· · ·O(3)	2.91	K(3)· · ·N(5)	2.80
K(2)· · ·O(3′)	2.98		
K(2)· · ·O(4)	2.80	K(4)· · ·O(2)	2.89
K(2)· · ·N(1)	3.09	K(4)· · ·O(3)	2.88
K(2)· · ·N(3)	2.81	K(4)· · ·O(5)	3.01
K(2)· · ·N(4)	3.21	K(4)· · ·O(6)	2.97
K(2)· · ·N(5)	2.95	K(4)· · ·N(2)	2.96
K(2)· · ·N(6)	3.20	K(4)· · ·N(3)	2.88
K(2)· · ·N(6′)	3.26	K(4)· · ·N(4)	2.93
		K(4)· · ·N(5)	2.94

tropic to varying degrees; however, their thermal amplitudes are by no means extreme.

The Water Molecules

The water molecules have quite normal geometries. That containing O(5) has O–H distances of 0.73(5) and 0.76(5) Å, with an H–O–H angle of 106(3)°. That containing O(6) has O–H distances of 0.80(4) and 0.90(4) Å, with an H–O–H angle of 111(3)°. In both cases, the principal axis of thermal motion of the oxygen atom is essentially normal to the molecular plane.

Acknowledgements

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