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The Crystal Structure of μ-Amido-μ-superoxo-bis[tetraamminecobalt(III)] Tetranitrate, $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$

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The crystal and molecular structure of μ-amido-μ-superoxo-bis[tetraamminecobalt(III)] tetranitrate, $(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4{}^{4+}\cdot 4NO_3{}^-$, has been determined by X-ray crystallographic analysis. The green-black salt crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 8.451 \pm 0.003$ Å, $b = 13.196 \pm 0.006$ Å, $c = 17.304 \pm 0.003$ Å, $\beta = 103.90 \pm 0.03°$, and $Z = 4$. The measured density is 1.95 ± 0.01 g/cm^3; the calculated density is 1.947 ± 0.001 g/cm^3. Intensity data were collected with a Datex-automated General Electric diffractometer using Fe Kα radiation. The structure was determined by Patterson methods and refined by three-dimensional Fourier and least-squares techniques. Refinement of all positional and thermal parameters (hydrogen atoms isotropic) yielded a final R index of 0.051 for 1888 reflections. The coordinating ligands form nearly regular octahedra about the cobalt atoms, with Co–N and Co–O distances of about 1.96 and 1.87 Å. The five-membered ring Co–N–Co–O–O– is very nearly planar; the O–O distance is 1.32 Å, and the Co–N–Co and Co–O–O angles are 115 and 120°, respectively. This geometry indicates that the O_2 bridge is a superoxo rather than a peroxo group.

Introduction

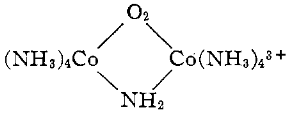
Dinuclear cobalt complexes have been known for some time; the major analytical, preparative, and constitutional work was carried out by Alfred Werner and his coworkers at about the turn of the century. These compounds may be prepared with from one to three bridging groups which can be one or more of the following: OH^-, $NH_2{}^-$, CH_3COO^-, $NO_2{}^-$, $SO_4{}^{2-}$, $C_2O_4{}^{2-}$, $O_2{}^{2-}$, $O_2{}^-$, and O_2H^-.

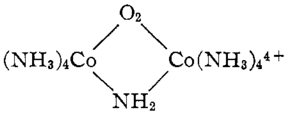
The compounds containing O_2 bridges are of particular interest as they exhibit involved oxidation–reduction behavior and complicated interconversion reactions which may have relevance to the understanding of the behavior of biologically important molecular oxygen carriers. Our particular interest in these compounds stemmed from the unresolved nature of the bonding in and the configuration of the O_2 bridge and from the several different structures for these bridged cations that had been proposed in the literature.

The following monobridged and analogous dibridged dicobalt complexes were investigated by Werner[1,2]

$(NH_3)_5Co—O_2—Co(NH_3)_5{}^{4+}$
I

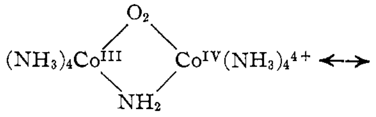
$(NH_3)_5Co—O_2—Co(NH_3)_5{}^{5+}$
II

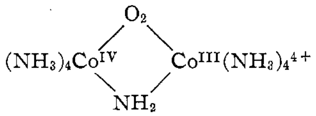

III


IV

The salts of I and III are generally red or brown and those of II and IV are dark green. In Werner's formulation the O_2 groups in all of these complexes were assumed to be peroxo groups. This formulation quite satisfactorily resulted in the cobalt atoms in I and III all being tervalent, but it required that II and IV each contain one tervalent and one tetravalent cobalt atom. Werner was unable to give any further proof of the existence of tetravalent cobalt.

The cations II and IV were shown by Gleu[3] and Malatesta[4] to be paramagnetic with a magnetic moment consistent with the presence of one unpaired electron. Esr studies of II and IV in solution have demonstrated that the unpaired electron spends an equal fraction of its time on each cobalt atom.[5,6] This suggests that IV, for example, may be a resonance hybrid of V and VI, with each cobalt atom having a valency intermediate between three and four,[4] or, alternatively, that the unpaired electron may occupy a molecular orbital which, although centered on the O_2 bridge, extends well onto the cobalt atoms. In the first formulation the O_2 bridge is still a peroxide group, as was originally assumed, but in the second case the bridge possesses more the character of an $O_2{}^-$, or superoxide, group.


V


VI

On the basis of single-crystal esr measurements, Goodman, Hecht, and Weil[7] tentatively predicted that the O_2 bridge in IV would be σ bonded to each of the cobalt atoms and oriented skew to the Co–Co axis, as indicated in Figure 1a. This configuration is quite

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[1] A. Werner and A. Mylius, *Z. Anorg. Allgem. Chem.*, **16**, 245 (1898).
[2] A. Werner, *Ann. Chem.*, **375**, 1 (1910).
[3] K. Gleu, *Angew. Chem.*, **48**, 470 (1935).
[4] L. Malatesta, *Gazz. Chim. Ital.*, **73**, 287 (1942).
[5] I. Bernal, E. A. B. Ebsworth, and J. A. Weil, *Proc. Chem. Soc.*, 57 (1959).
[6] E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).
[7] G. Goodman, H. Hecht, and J. A. Weil, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 90.

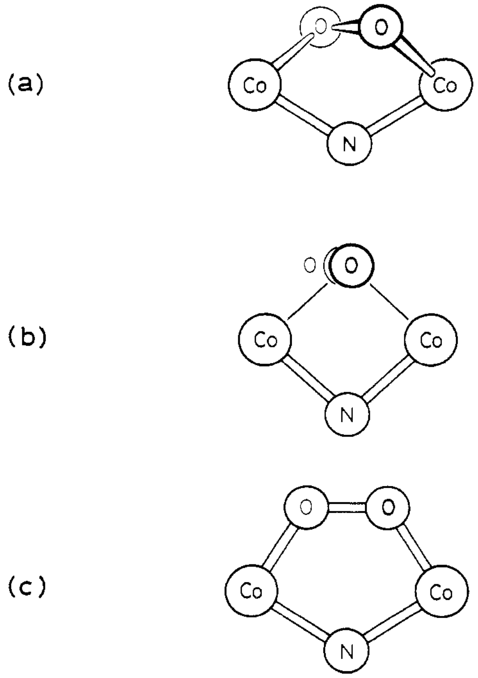


Figure 1.—The proposed configurations of the ring formed by the two cobalt atoms and the two bridges. The ammine groups coordinated to the cobalt atoms have been omitted for clarity: (a) the configuration expected when the O_2 bridge is a σ-bonded peroxide group; (b) the configuration expected if the O_2 bridge is considered to be perpendicular to the Co–N–Co plane and π bonded to the cobalt atoms; (c) the planar configuration predicted assuming the O_2 bridge to be a superoxide group, which was confirmed by this study.

close to what would be expected if the O_2 bridge were a peroxide group; the five-membered ring formed by the two cobalt atoms and the atoms of the bridges would have to be decidedly nonplanar in order to accommodate the relatively large dihedral angle expected for a peroxide group.

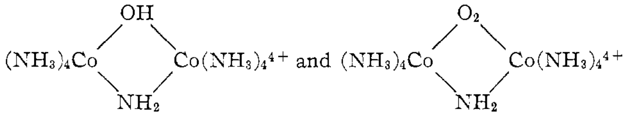
From steric considerations and electrochemical data Vlček proposed that the most probable configuration for IV would be one in which the O_2 bridge is oriented perpendicular to the Co–Co axis and bonded to the cobalt atoms by the overlap of its π orbitals with the cobalt d orbitals[8] (Figure 1b). Such π bonding would presumably be similar to that found in metal–olefin complexes, in the iridium–oxygen complexes studied by Ibers,[9] or in the anion of K_3CrO_8; this last was interpreted by Pauling as containing four O_2 groups having mostly superoxide character.[10]

A third configuration, with the O_2 bridge coplanar with the Co–N–Co grouping (Figure 1c), would result if the O_2 bridge were assumed to be a σ-bonded superoxide group. Such a configuration would further be in agreement with the planar bridge structure recently reported for the cation of the analogous monobridged compound, II.[11,12]

This structural study was undertaken in order to determine the exact configuration of cation IV and in particular to determine the geometry of the O_2 bridge.

Experimental Section

Vortmann's sulfate, a mixture containing the cations



$$(NH_3)_4Co(\mu\text{-}OH)(\mu\text{-}NH_2)Co(NH_3)_4{}^{4+} \text{ and } (NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4{}^{4+}$$

was prepared by the method given by Werner,[13] and from it samples of μ-amido-μ-superoxo-bis[tetraamminecobalt(III)]tetranitrate were extracted with concentrated nitric acid. The samples obtained were washed with a little dilute nitric acid, then with alcohol, and then dried. Crystals of the compound were prepared by allowing a test tube of hot, saturated nitrate solution about 2 *F* in nitric acid to cool slowly overnight in a thermos of hot water. The dark green-black crystals grown in this fashion were generally extremely thin blades which appeared to be hollow. A number of smaller, slightly stockier blades were also formed from which the crystals used in this structure analysis were chosen.

The compound was also found to crystallize in a second modification from more acidic nitric acid solutions (*ca.* 8–10 *F*). These crystals were obtained in the form of small "stars" consisting of about 12 needlelike crystals radiating from a central point. Weissenberg photographs of single needles of these crystals indicated that they were all twinned. They were monoclinic with approximate unit cell dimensions: $a = 8.0$, $b = 18.6$, $c = 12.4$ Å. The monoclinic angle was not determined, but it is quite close to 90°.

The space group $P2_1/c$ was indicated by the systematic absences on Weissenberg photographs of reflections $h0l$ with l odd and $0k0$ with k odd. The cell constants were determined by a least-squares fit to measurements of 2θ for 67 reflections on photographs prepared with a special camera which holds the film in the asymmetric position. The resulting values, their standard deviations, and related data are: $a = 8.451 \pm 0.003$ Å, $b = 13.196 \pm 0.006$ Å, $c = 17.304 \pm 0.003$ Å, $\beta = 103.90 \pm 0.03°$, $\lambda(\text{Cu K}\alpha_1)$ 1.54051 Å, $\lambda(\text{Cu K}\alpha_2)$ 1.54433 Å), $V = 1873$ Å^3, and $T = 26°$. The density calculated for four formula units of $Co_2(NH_2,O_2)(NH_3)_8(NO_3)_4$ per unit cell is 1.947 ± 0.001 g cm^{-1}; the density determined by flotation in a carbon tetrachloride–1,2-dibromoethane solution is 1.95 ± 0.01 g cm^{-1}.

A nearly rectangular prism about 0.05 × 0.07 × 0.04 mm in size was used for the collection of three-dimensional intensity data. The intensities were measured using a θ–2θ scan at a scanning speed of 1°/min. Background was counted for 100 sec at each end of the scan. The scan range of about 2° was adjusted to account for α_1–α_2 splitting. The takeoff angle used was 3°; a check of several high-angle reflections showed that our settings included the entire peak in the scan.

Iron radiation ($\lambda(\text{K}\alpha)$ 1.9373 Å) filtered with a single thickness of Du Pont manganese dioxide (General Electric Part No. 257) was used to reduce absorption and fluorescence effects. The temperature in the laboratory containing the diffractometer was fairly constant at 27° throughout the collection of the data.

A moderately strong reflection, 225, was chosen as a "check" reflection and was remeasured after every 15 reflections. There were no significant deviations in the intensity of this reflection during the collection of the data, which required approximately 12 days of 24-hr operation. Of the 1993 measured reflections, 1888 were calculated as greater than zero and were used in the refinement of the structure.

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(8) A. A. Vlček, *Trans. Faraday Soc.*, **56**, 1137 (1960).

(9) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(10) L. Pauling, "The Nature of the Chemical Bond," 34th ed, Cornell University Press, Ithaca, N. Y., 1960, pp 351, 352.

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

(12) R. E. Marsh and W. P. Schaefer, *ibid.*, **B24**, 246 (1968).

(13) A. Werner, *Ber.*, **40**, 4609 (1907).

Treatment of the Data

The values for the observed intensities, I_{obsd}, were derived from the scaler counts using the formula

$$I_{\text{obsd}} = S - \frac{B_1 + B_2}{2}\left(\frac{t}{100}\right)$$

where S is the scan count, B_1 and B_2 are the two background counts, and t is the scan time in seconds. Negative values of I_{obsd} calculated from this formula were set equal to zero.

The standard deviation for each reflection was calculated using

$$\sigma^2(I_{\text{obsd}}) = S + \frac{B_1 + B_2}{2}\left(\frac{t}{100}\right)^2 + (0.03S)^2$$

The last term in this equation is an empirical term (Busing and Levy[14]) which presumably allows for errors not due to counting statistics. The intensities and their standard deviations were corrected for Lorentz and polarization factors but not for absorption. The value of μ for this compound is 59 cm^{-1}, and neglect of this correction could have led to errors of 4% in the structure factors in the extreme case. The standard deviations calculated in this way were the basis for the weights used in the least-squares refinement.

Determination and Refinement of the Structure

A three-dimensional Patterson synthesis was calculated and from it the approximate coordinates of the cobalt atoms were found. Structure factors calculated on the basis of these coordinates led to an R index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.44. A three-dimensional electron density synthesis was then computed; all of the nonhydrogen atoms were apparent in this synthesis, and two cycles of full-matrix, least-squares refinement of the coordinates and isotropic temperature factors of all of these atoms reduced the R index to 0.11. Introducing anisotropic temperature factors for the cobalt atoms further reduced the R index to 0.10. At this point difference maps were calculated in the planes where the hydrogen atoms of the NH_3 groups were expected; nearly all of the hydrogen atoms were apparent, and they were included in subsequent calculations.

In subsequent least-squares cycles, 367 parameters—a scale factor, a secondary extinction factor,[15] positional parameters of all of the atoms, anisotropic temperature factors for the nonhydrogen atoms, and isotropic temperature factors for the hydrogen atoms—were adjusted. Because of the storage limitations of the computer, these 367 parameters were apportioned among four complete matrices.

All calculations were carried out on an IBM 7094 computer using subprograms operating under the CRYM crystallographic computing system. The quantity minimized in the least-squares calculations was $\Sigma w(F_o^2 - F_c^{*2})^2$, where $w = 1/\sigma^2(F_o^2)$, and F_c^* is as defined by Larson's eq 3.[15b] Atomic form factors for cobalt, nitrogen, and oxygen were taken from ref 16, the values for Co being reduced by 1.74 electrons to take account of anomalous dispersion,[17] and the form factor for hydrogen was that calculated by Stewart, Davidson, and Simpson.[18]

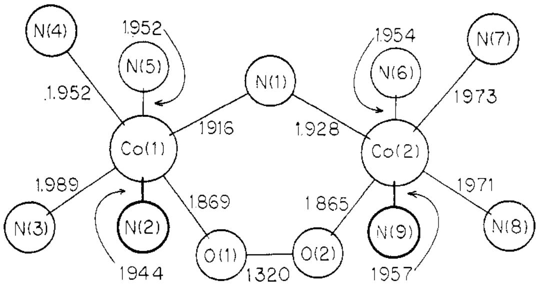

Figure 2.—Bond distances for the cation.

In the final cycle, no heavy-atom parameter shifted by as much as 0.5 esd. The final R index for 1888 "observed" reflections was 0.051, and the goodness of fit, $[\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, was 1.32. The final value of the secondary extinction parameter g, as defined by Larson's eq 3,[15b] was $(1.25 \pm 0.19) \times 10^{-6}$.

Table I contains the observed and calculated structure factors. The final parameters and their standard deviations for the heavy atoms are given in Table II, and the parameters of the hydrogen atoms are given in Table III.

The estimated standard deviations in the positions of the cobalt atoms are approximately 0.001 Å, while the esd's for the ammine nitrogen atoms and the bridge oxygen atoms are about 0.004 Å. The estimated standard deviations in the positions of the nitrate group atoms are roughly 0.008 Å, but these are not especially meaningful because the vibrational amplitudes for some of the nitrate oxygen atoms exceed 0.4 Å.

Description and Discussion of the Structure

Contrary to the predictions of Goodman, Hecht, and Weil[7] and of Vlček,[8] the O_2 bridge is very nearly coplanar with the cobalt atoms; the sum of the angles in the ring formed by the cobalt atoms and the bridges is 539.6°, only 0.4° from the total expected for a planar, five-membered ring. The two oxygen atoms each lie 0.045 Å from, and on opposite sides of, the Co–N–Co plane. Since these distances are roughly 10 times the estimated standard deviations in the oxygen positions, the distortion is real; it is probably due mainly to bond-angle strain in the five-membered ring.

The bond distances for the μ-amido-μ-superoxo-bis[tetraamminecobalt(III)] cation are shown in Figure 2;

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

[15] (a) W. H. Zachariasen, *Acta Cryst.*, **16**, 1139 (1963); (b) A. Larson, *ibid.*, **23**, 664 (1967).

[16] "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, pp 202–204.

[17] D. Cromer, *Acta Cryst.*, **18**, 17 (1965). $\Delta f' = -1.74$ electrons; $\Delta f'' = 0.8$ electron was ignored in this centric structure.

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

TABLE I[a]

H 0 0			
0	---	**	11195
H 1 0			
1	993	11	983
2	640	8	-630
3	172	8	165
4	1047	13	1058
5	201	11	184
6	844	12	832
7	446	9	511
8	65	14	78
H 2 0			
0	1648	26	-1647
1	389	6	-391
2	263	7	281
3	90	13	-95
4	91	16	88
5	271	10	282
6	349	10	-348
7	374	9	375
8	186	7	203
H 3 0			
1	1587	18	-1638
2	236	7	266
3	499	8	-526
4	433	8	-448
5	170	13	188
6	128	16	-132
7	344	9	-323
8	512	7	522
H 4 0			
0	693	13	-707
1	312	7	-304
2	924	11	-904
3	686	10	688
4	552	9	-549
5	90	21	-88
6	669	10	664
7	286	8	-266
H 5 0			
1	349	7	328
2	468	8	-445
3	88	17	45
4	140	14	142
5	602	10	-611
6	109	17	-73
7	34	36	-7
H 6 0			
0	142	15	145
1	1014	12	1007
2	573	9	565
3	627	10	-623
4	514	10	501
5	120	18	-137
6	402	9	-395
7	46	19	54
H 7 0			
1	161	11	-159
2	941	12	946
3	315	9	292
4	65	28	59
5	914	12	923
6	105	15	117
7	105	7	99
H 8 0			
0	336	13	-291
1	513	9	-530
2	1004	13	-1033
3	61	28	26
4	565	10	-586
5	88	19	103
6	363	7	363
H 9 0			
1	181	13	166
2	586	10	-576
3	360	10	-367
4	112	17	-120
5	540	9	-545
6	137	6	-136
H 10 0			
0	250	16	-253
1	197	12	202
2	341	10	352
3	189	12	-208
4	384	8	379
5	---	**	13
H 11 0			
1	268	10	-261
2	374	9	374
3	166	10	189
4	47	18	-2
H 12 0			
0	361	11	337
1	32	39	-13
2	148	10	-144
3	115	9	85
H 13 0			
1	116	8	131
H 1 1			
-8	208	10	-197
-7	---	**	-2
-6	429	13	-405
-5	615	14	-622
-4	290	11	-264
-3	463	11	-485
-2	60	20	82
-1	94	12	-140
0	50	17	31
1	249	8	274
2	577	11	535
3	149	13	-153
4	470	12	498
5	171	18	-213
6	192	17	203
7	94	24	-116
8	172	9	190
H 2 1			
-8	119	13	137
-7	293	13	265
-6	289	15	308
-5	168	17	140
-4	84	22	-61
-3	786	14	787
-2	533	11	-571
-1	582	11	-551
0	625	11	-635
1	648	12	-676
2	63	22	22
3	1594	25	-1587
4	531	12	-505
5	211	16	-204
6	344	14	342
7	21	50	-22
8	76	13	69
H 3 1			
-8	86	14	75
-7	189	15	190
-6	692	15	691
-5	542	13	541
-4	338	12	350
-3	502	11	-505
-2	---	**	-19
-1	514	10	487
0	488	10	468
1	383	10	372
2	413	10	-414
3	---	**	13
4	848	16	-879
5	113	24	120
6	---	**	-82
7	108	21	147
H 4 1			
-7	223	13	-214
-6	241	15	-210
-5	55	39	85
-4	---	**	48
-3	265	12	257
-2	250	10	237
-1	1033	17	1071
0	253	10	232
1	876	15	874
2	48	28	76
3	441	12	429
4	137	20	190
5	123	23	-146
6	360	13	-349
7	34	37	68
H 5 1			
-7	103	16	-84
-6	335	13	-387
-5	345	14	-348
-4	85	27	80
-3	522	12	-525
-2	608	12	-647
-1	155	13	151
0	630	12	625
1	117	16	-145
2	650	13	668
3	253	13	-255
4	499	13	508
5	615	15	646
6	95	26	117
7	156	13	168
H 6 1			
-7	---	**	-7
-6	53	37	-89
-5	423	13	-421
-4	234	16	201
-3	166	17	-162
-2	49	33	30
-1	476	11	-451
0	229	12	-246
1	878	16	-858
2	54	31	-50
3	111	22	-151
4	47	42	63
5	81	30	5
6	97	22	25
7	46	23	-38
H 7 1			
-7	67	16	-50
-6	268	12	249
-5	109	25	105
-4	99	27	-119
-3	532	13	554
-2	43	39	-34
-1	97	22	-76
0	---	**	-6
1	266	12	-316
2	321	12	-312
3	282	13	-269
4	246	15	-270
5	241	15	-231
6	84	22	-92
H 8 1			
-6	70	23	33
-5	356	12	346
-4	204	16	-202
-3	594	14	-610
-2	314	14	305
-1	116	23	140
0	250	14	-241
1	201	16	207
2	501	13	-505
3	484	13	-471
4	184	18	150
5	107	21	-97
6	123	13	115
H 9 1			
-6	178	9	179
-5	215	13	206
-4	437	13	427
-3	56	39	-71
-2	186	18	-171
-1	235	15	220
0	468	13	-466
1	195	17	-215
2	136	23	-157
3	380	13	-368
4	214	15	-216
5	51	30	64
H 10 1			
-5	108	14	-101
-4	135	18	118
-3	217	16	220
-2	292	16	-164
-1	117	23	88
0	56	39	51
1	---	**	22
2	441	13	434
3	337	13	340
4	81	23	55
5	62	18	49
H 11 1			
-4	530	11	-543
-3	170	15	-182
-2	---	**	-21
-1	257	13	-241
0	407	12	394
1	200	15	208
2	88	24	33
3	349	12	337
4	100	14	86
H 12 1			
-3	417	10	-422
-2	28	38	50
-1	429	11	-437
0	195	13	-161
1	152	14	-120
2	119	15	-130
3	293	9	-287
H 13 1			
-1	334	9	343
0	---	**	-36
1	148	9	160
H 0 2			
-8	726	14	727
-7	---	**	-68
-6	75	33	64
-5	410	13	425
-4	680	13	-716
-3	924	16	-944
-2	606	11	-591
-1	1720	27	-1829
0	564	10	-570
1	1145	18	1155
2	1824	28	-1920
3	557	12	-518
4	---	**	54
5	287	14	-304
6	242	15	244
7	384	12	368
H 1 2			
-8	316	10	324
-7	537	13	528
-6	---	**	35
-5	702	14	719
-4	765	14	797
-3	100	17	-106
-2	1914	30	1930
-1	529	10	532
0	773	13	-780
1	47	22	29
2	819	14	-828
3	1266	21	-1284
4	206	14	-204
5	547	14	-557
6	435	13	-453
7	128	18	121
H 2 2			
-8	371	10	-374
-7	189	16	193
-6	75	32	67
-5	376	13	-360
-4	656	13	660
-3	494	11	-502
-2	166	11	-133
-1	1714	27	1616
0	344	9	353
1	635	12	646
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-5	465	11	-465
-4	260	12	-256
-3	77	26	11
-2	296	13	-240
-1	127	20	130
0	44	37	15
1	483	12	478
2	280	10	283
3	362	12	373
H 6 13			
-5	192	10	-211
-4	96	18	-89
-3	90	22	-31
-2	113	19	-103
-1	354	12	-345
0	---	**	-48
1	272	11	-274
2	33	30	-17
H 7 13			
-4	91	16	-90
-3	151	13	165
-2	81	21	56
-1	324	11	-326
0	172	12	-166
1	90	16	69
H 8 13			
-3	249	9	-248
-2	82	16	52
-1	---	**	24
0	---	**	-40
H 0 14			
-6	171	11	-177
-5	73	23	45
-4	149	17	-164
-3	265	13	-279
-2	319	13	277
-1	403	13	-409
0	620	14	-608
1	194	14	200
2	373	11	-368
3	263	17	-292
H 1 14			
-6	140	12	150
-5	97	20	87
-4	490	12	477
-3	---	**	-51
-2	84	28	-96
-1	344	13	351
0	640	14	-642
1	272	13	-269
2	195	13	210
3	375	15	-366
H 2 14			
-6	252	10	236
-5	73	23	-85
-4	132	18	113
-3	475	13	500
-2	151	17	-167
-1	472	13	488
0	649	14	653
1	205	13	-213
2	315	11	335
3	168	29	157
H 3 14			
-6	---	**	-36
-5	139	15	140
-4	323	12	-312
-3	274	13	271
-2	52	35	-42
-1	456	12	-469
0	299	12	243
1	78	24	64
2	228	12	-234
H 4 14			
-5	228	11	231
-4	81	24	122
-3	227	13	-203
-2	335	12	346
-1	194	14	-179
0	305	12	-307
1	314	11	330
2	83	26	46
H 5 14			
-5	214	11	-240
-4	141	15	156
-3	260	12	-269
-2	130	17	-123
-1	218	13	214
0	151	15	-172
1	32	38	-49
2	195	20	206
H 6 14			
-4	72	21	-92
-3	222	11	-199
-2	646	13	-637
-1	53	26	-60
0	---	**	-30
1	258	13	-253
H 7 14			
-3	33	33	39
-2	137	14	148
-1	416	11	-416
0	120	18	92
H 1 15			
-5	144	13	144
-4	177	13	153
-3	67	27	5
-2	50	35	62
-1	227	13	-206
0	135	18	-115
1	96	24	-60
2	192	26	-184
H 2 15			
-5	51	35	52
-4	109	20	134
-3	271	12	-286
-2	415	12	410
-1	126	18	133
0	481	12	506
1	46	37	14
2	58	67	15
H 3 15			
-5	124	23	-146
-4	342	12	-346
-3	98	22	-111
-2	81	24	-60
-1	401	12	411
0	247	14	259
1	472	13	477
H 4 15			
-5	243	18	-241
-4	97	25	-83
-3	156	17	-149
-2	416	12	-417
-1	351	12	-368
0	471	12	-492
1	386	16	-408
H 5 15			
-4	150	21	152
-3	156	17	157
-2	48	34	-2
-1	258	13	-283
0	117	24	-131
1	382	25	-401
H 6 15			
-3	384	16	412
-2	303	15	323
-1	103	32	140
0	72	63	55
H 0 16			
-5	99	27	-87
-4	528	12	530
-3	168	13	-166
-2	320	11	334
-1	955	**	579
0	164	23	-172
1	326	26	360
H 1 16			
-5	562	18	-565
-4	113	21	98
-3	225	14	252
-2	244	**	-109
-1	---	**	60
0	260	17	260
1	328	27	-345
H 2 16			
-4	353	18	-387
-3	170	21	174
-2	109	29	-132
-1	338	16	-339
0	65	46	46
1	172	54	-188
H 3 16			
-4	231	**	57
-3	---	**	32
-2	400	14	396
-1	155	22	-162
0	---	**	58
H 4 16			
-3	134	36	-125
-2	56	56	-133
-1	192	27	211
0	---	**	-140
H 5 16			
-2	138	51	-197
-1	177	52	221
H 1 17			
-3	80	54	-11
-2	81	67	-88
-1	96	74	122
H 2 17			
-3	315	35	-371
-2	208	44	-222
-1	80	97	-137

[a] The four parts in each column are *h*, $10F_o$, $10\sigma(F_o)$, and $10F_c$. The symbol --- in the F_o column indicates that F_o was assigned the value 0; asterisks in the column of standard deviations indicate the reflections were not used in the refinement.

the angles are listed in Table IV. The O–O distance of 1.320 Å is not significantly different from the values 1.317 and 1.312 Å found for the O–O distance in two salts of the analogous singly bridged superoxo cation[11,12] and is very close to the 1.28-Å O–O distance found for the superoxide ion.[10] Pauling considers the superoxide oxygen–oxygen bond as a combination of a single (σ) bond and a three-electron (π) bond.[10] Since two orbitals are utilized in the oxygen–oxygen bond, it is impossible for this anion to form any type of bridged compound other than a planar one.

Interpreting the O_2 bridge in this compound as a superoxo bridge satisfactorily accounts for the observed esr spectra since the unpaired electron can be expected to be delocalized over the bridge so that it can interact equally with the nuclear spins of both cobalt atoms. Recent esr measurements by Weil and Kinnaird on samples of this compound, in which ^{17}O was incorpo-

TABLE II

POSITIONAL AND THERMAL PARAMETERS OF THE HEAVY ATOMS[a]

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(1)	6565(.9)	2598(.6)	974(.5)	63(1)	24(.5)	11(.3)	-1(1)	10(1)	1(1)
Co(2)	9493(1)	1854(.6)	2440(.5)	65(1)	26(.6)	12(.3)	5(1)	8(1)	-1(1)
O(1)	8310(4)	3452(3)	1420(2)	72(6)	30(2)	16(2)	-12(6)	0(5)	2(3)
O(2)	9447(4)	3174(3)	2050(2)	87(6)	33(3)	15(1)	-17(7)	-10(5)	3(3)
N(1)	7469(5)	1528(3)	1693(2)	65(7)	22(3)	14(2)	0(7)	11(6)	7(3)
N(2)	7678(5)	2114(3)	184(3)	103(8)	42(3)	17(2)	16(8)	30(6)	-2(4)
N(3)	5790(6)	3781(4)	272(3)	103(8)	49(4)	24(2)	23(9)	20(7)	24(4)
N(4)	4674(5)	1765(4)	496(3)	79(8)	43(3)	22(2)	-6(8)	14(6)	-9(4)
N(5)	5362(5)	3162(3)	1706(3)	102(8)	24(3)	18(2)	12(8)	30(6)	4(4)
N(6)	8350(5)	2308(4)	3235(3)	87(7)	55(4)	14(2)	5(9)	18(6)	-2(4)
N(7)	9644(6)	484(3)	2908(3)	126(9)	30(3)	28(2)	17(8)	13(7)	14(4)
N(8)	11537(5)	2274(4)	3186(3)	78(7)	48(3)	23(2)	14(9)	-7(6)	-9(4)
N(9)	10752(5)	1435(4)	1682(3)	90(8)	48(3)	20(2)	2(8)	25(6)	-9(4)
N(10)	10989(6)	778(4)	-587(3)	136(10)	37(4)	43(3)	-5(9)	57(8)	6(5)
O(3)	10988(5)	1629(3)	-285(3)	176(9)	30(3)	37(2)	-12(8)	33(7)	-18(4)
O(4)	11658(7)	64(4)	-177(4)	253(12)	54(4)	108(4)	70(11)	46(12)	53(7)
O(5)	10297(8)	652(4)	-1297(3)	488(18)	72(4)	28(2)	-145(13)	74(10)	-25(5)
N(11)	4690(6)	766(4)	3040(3)	117(9)	34(3)	34(3)	8(9)	62(8)	-1(5)
O(6)	3519(5)	317(3)	3190(3)	150(9)	58(3)	87(3)	50(9)	153(9)	76(6)
O(7)	6055(6)	687(4)	3490(3)	139(9)	93(4)	36(2)	29(10)	0(7)	5(5)
O(8)	4475(5)	1317(3)	2434(3)	154(8)	49(3)	32(2)	3(8)	64(7)	31(4)
N(12)	11254(6)	1243(3)	5097(3)	97(9)	36(3)	28(2)	-2(9)	7(7)	17(4)
O(9)	9750(5)	1209(3)	4786(2)	100(8)	51(3)	31(2)	13(7)	10(6)	5(4)
O(10)	11766(5)	1558(4)	5783(2)	166(9)	74(4)	18(2)	1(9)	-6(6)	-9(4)
O(11)	12210(5)	990(4)	4685(3)	118(7)	84(4)	28(2)	57(9)	59(6)	5(4)
N(13)	4606(7)	3951(4)	3513(3)	230(12)	53(4)	15(2)	23(12)	13(9)	-4(5)
O(12)	4743(9)	4555(4)	4056(3)	476(19)	66(4)	50(3)	28(14)	-1(12)	-20(6)
O(13)	5135(5)	3087(3)	3647(3)	184(9)	54(3)	41(2)	95(9)	-35(7)	-16(5)
O(14)	3623(7)	4186(4)	2877(3)	276(13)	89(5)	42(3)	83(12)	24(9)	12(6)

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

TABLE III

POSITIONAL AND THERMAL PARAMETERS OF THE HYDROGEN ATOMS[a]

Atom	x	y	z	B(Å^2)
H(1)	668(5)	129(3)	191(3)	1.2(1.0)
H(2)	760(5)	96(3)	144(3)	1.6(1.0)
H(3)	704(9)	214(6)	-27(4)	7.6(2.0)
H(4)	807(7)	158(4)	23(3)	3.1(1.3)
H(5)	851(7)	253(5)	14(3)	3.8(1.3)
H(6)	646(11)	436(7)	57(6)	9.9(2.5)
H(7)	624(9)	389(5)	-8(4)	5.8(1.8)
H(8)	497(9)	392(5)	22(4)	5.2(1.7)
H(9)	375(8)	196(5)	49(4)	5.4(1.7)
H(10)	487(8)	141(5)	11(4)	4.5(1.5)
H(11)	462(10)	123(6)	80(5)	8.8(2.3)
H(12)	589(7)	378(4)	198(3)	3.6(1.3)
H(13)	444(7)	338(4)	147(3)	3.5(1.3)
H(14)	509(5)	273(4)	202(3)	1.9(1.1)
H(15)	812(10)	297(6)	336(5)	8.0(2.1)
H(16)	744(8)	220(5)	320(4)	5.5(1.8)
H(17)	875(7)	206(4)	374(3)	3.4(1.3)
H(18)	910(12)	21(7)	287(6)	10.9(3.1)
H(19)	1048(14)	47(8)	339(6)	13.2(3.4)
H(20)	1051(13)	-6(8)	277(6)	12.1(3.3)
H(21)	1204(10)	173(7)	358(5)	9.7(2.5)
H(22)	1144(11)	279(7)	335(6)	9.8(2.9)
H(23)	1199(11)	233(8)	303(6)	10.7(3.0)
H(24)	1059(9)	85(6)	144(5)	8.1(2.1)
H(25)	1192(9)	122(5)	198(4)	5.8(1.7)
H(26)	1087(10)	179(6)	145(5)	7.4(2.1)

[a] Values of x, y, and z have been multiplied by 10^3.

TABLE IV

DISTANCES AND ANGLES IN THE CATION[a]

Atoms	Distance, Å	Atoms	Angle, deg
Co(1)–Co(2)	3.242 (1)	N(2)–Co(1)–N(3)	88.4 (2)
O(1)–O(2)	1.320 (5)	N(2)–Co(1)–N(4)	90.1 (2)
Co(1)–O(1)	1.869 (4)	N(2)–Co(1)–N(5)	175.6 (2)
Co(1)–N(1)	1.916 (4)	N(3)–Co(1)–N(4)	93.9 (2)
Co(1)–N(2)	1.944 (5)	N(3)–Co(1)–N(5)	87.2 (2)
Co(1)–N(3)	1.989 (5)	N(4)–Co(1)–N(5)	89.4 (2)
Co(1)–N(4)	1.952 (5)	Co(1)–N(1)–Co(2)	114.9 (2)
Co(1)–N(5)	1.952 (4)	Co(1)–O(1)–O(2)	121.3 (3)
Co(2)–O(2)	1.865 (4)	Co(2)–O(2)–O(1)	120.4 (3)
Co(2)–N(1)	1.928 (4)	O(2)–Co(2)–N(1)	91.6 (2)
Co(2)–N(6)	1.954 (5)	O(2)–Co(2)–N(6)	89.9 (2)
Co(2)–N(7)	1.973 (5)	O(2)–Co(2)–N(7)	176.6 (2)
Co(2)–N(8)	1.971 (5)	O(2)–Co(2)–N(8)	85.0 (2)
Co(2)–N(9)	1.957 (5)	O(2)–Co(2)–N(9)	89.4 (2)
		N(1)–Co(2)–N(6)	91.8 (2)
Atoms	Angle, deg	N(1)–Co(2)–N(7)	91.7 (2)
		N(1)–Co(2)–N(8)	176.6 (2)
O(1)–Co(1)–N(1)	91.4 (2)	N(1)–Co(2)–N(9)	91.5 (2)
O(1)–Co(1)–N(2)	91.2 (2)	N(6)–Co(2)–N(7)	89.2 (2)
O(1)–Co(1)–N(3)	83.7 (2)	N(6)–Co(2)–N(8)	87.5 (2)
O(1)–Co(1)–N(4)	177.2 (2)	N(6)–Co(2)–N(9)	176.7 (2)
O(1)–Co(1)–N(5)	89.1 (2)	N(7)–Co(2)–N(8)	91.6 (2)
N(1)–Co(1)–N(2)	91.7 (2)	N(7)–Co(2)–N(9)	91.3 (2)
N(1)–Co(1)–N(3)	175.1 (2)	N(8)–Co(2)–N(9)	89.2 (2)
N(1)–Co(1)–N(4)	91.0 (2)		
N(1)–Co(1)–N(5)	92.7 (2)		

[a] Values in parentheses are estimated standard deviations in the last digits.

TABLE V

BOND DISTANCES AND ANGLES WITHIN THE NITRATE GROUPS

Atoms	Distance, Å	Atoms	Angle, deg
N(10)–O(3)	1.238 (7)	O(3)–N(10)–O(4)	119.8 (6)
N(10)–O(4)	1.232 (8)	O(3)–N(10)–O(5)	119.5 (5)
N(10)–O(5)	1.239 (8)	O(4)–N(10)–O(5)	120.5 (6)
N(11)–O(6)	1.234 (7)	O(6)–N(11)–O(7)	120.2 (5)
N(11)–O(7)	1.231 (7)	O(6)–N(11)–O(8)	119.5 (5)
N(11)–O(8)	1.253 (7)	O(7)–N(11)–O(8)	120.3 (5)
N(12)–O(9)	1.256 (6)	O(9)–N(12)–O(10)	120.7 (5)
N(12)–O(10)	1.233 (6)	O(9)–N(12)–O(11)	118.2 (5)
N(12)–O(11)	1.245 (7)	O(10)–N(12)–O(11)	121.0 (5)
N(13)–O(12)	1.216 (8)	O(12)–N(13)–O(13)	120.1 (5)
N(13)–O(13)	1.226 (7)	O(12)–N(13)–O(14)	115.0 (6)
N(13)–O(14)	1.248 (8)	O(13)–N(13)–O(14)	122.1 (5)
Av	1.238	Av dev from 120°	1.0
σ	0.011		

rated into the bridge, indicate that this is indeed the case;[19] the unpaired electron appears to reside in what amounts to a molecular orbital over the Co–O–O–Co atoms with the nodal plane coincident with the plane of the ring.

Thewalt and Marsh, in their study of the ethylenediamine form of this compound, have found the Co–O–O–Co–N– ring to be similarly planar although slightly more puckered than in the ammine-complexed form we have studied, with an O–O bond distance of 1.36 Å.[20] This slightly longer O–O distance is consistent with the larger deviation from planarity of the ring and the consequent weakening of the half-order bond.

There are four nitrate groups per asymmetric unit. The bond distances and angles within these groups are given in Table V. The average N–O distance for all of

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(19) J. A. Weil and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 3341 (1967).

(20) U. Thewalt and R. E. Marsh, *J. Am. Chem. Soc.*, **89**, 6364 (1967).

Table VI

Observed N–H Bond Distances and Their Standard Deviations

Atoms	Distance, Å	Atoms	Distance, Å
N(1)–H(1)	0.90 (5)	N(6)–H(15)	0.92 (8)
N(1)–H(2)	0.88 (4)	N(6)–H(16)	0.77 (7)
N(2)–H(3)	0.85 (8)	N(6)–H(17)	0.91 (6)
N(2)–H(4)	0.78 (6)	N(7)–H(18)	0.58 (11)
N(2)–H(5)	0.90 (6)	N(7)–H(19)	0.96 (11)
N(3)–H(6)	1.01 (9)	N(7)–H(20)	1.09 (11)
N(3)–H(7)	0.81 (8)	N(8)–H(21)	1.01 (9)
N(3)–H(8)	0.70 (7)	N(8)–H(22)	0.75 (9)
N(4)–H(9)	0.82 (7)	N(8)–H(23)	0.52 (10)
N(4)–H(10)	0.86 (6)	N(9)–H(24)	0.87 (8)
N(4)–H(11)	0.88 (9)	N(9)–H(25)	1.04 (7)
N(5)–H(12)	0.99 (6)	N(9)–H(26)	0.64 (8)
N(5)–H(13)	0.84 (6)		
N(5)–H(14)	0.86 (5)		

Table VII

Bond Angles (and Standard Deviations) Involving the Hydrogen Atoms

Atoms	Angle, deg	Atoms	Angle, deg
Co(1)–N(1)–H(1)	108 (3)	H(12)–N(5)–H(13)	102 (5)
Co(1)–N(1)–H(2)	112 (3)	H(12)–N(5)–H(14)	113 (5)
Co(2)–N(1)–H(1)	115 (3)	H(13)–N(5)–H(14)	101 (5)
Co(2)–N(1)–H(2)	109 (3)	Co(2)–N(6)–H(15)	109 (5)
H(1)–N(1)–H(2)	96 (4)	Co(2)–N(6)–H(16)	122 (5)
Co(1)–N(2)–H(3)	110 (5)	Co(2)–N(6)–H(17)	116 (4)
Co(1)–N(2)–H(4)	119 (4)	H(15)–N(6)–H(16)	113 (7)
Co(1)–N(2)–H(5)	112 (4)	H(15)–N(6)–H(17)	96 (6)
H(3)–N(2)–H(4)	109 (7)	H(16)–N(6)–H(17)	98 (6)
H(3)–N(2)–H(5)	104 (6)	Co(2)–N(7)–H(18)	124 (11)
H(4)–N(2)–H(5)	104 (6)	Co(2)–N(7)–H(19)	110 (6)
Co(1)–N(3)–H(6)	103 (5)	Co(2)–N(7)–H(20)	120 (5)
Co(1)–N(3)–H(7)	117 (5)	H(18)–N(7)–H(19)	119 (12)
Co(1)–N(3)–H(8)	117 (6)	H(18)–N(7)–H(20)	96 (12)
H(6)–N(3)–H(7)	87 (7)	H(19)–N(7)–H(20)	78 (9)
H(6)–N(3)–H(8)	107 (8)	Co(2)–N(8)–H(21)	114 (5)
H(7)–N(3)–H(8)	119 (8)	Co(2)–N(8)–H(22)	110 (7)
Co(1)–N(4)–H(9)	121 (5)	Co(2)–N(8)–H(23)	110 (11)
Co(1)–N(4)–H(10)	110 (4)	H(21)–N(8)–H(22)	117 (9)
Co(1)–N(4)–H(11)	111 (6)	H(21)–N(8)–H(23)	102 (12)
H(9)–N(4)–H(10)	121 (6)	H(22)–N(8)–H(23)	103 (13)
H(9)–N(4)–H(11)	94 (7)	Co(2)–N(9)–H(24)	122 (5)
H(10)–N(4)–H(11)	94 (7)	Co(2)–N(9)–H(25)	110 (4)
Co(1)–N(5)–H(12)	112 (3)	Co(2)–N(9)–H(26)	114 (7)
Co(1)–N(5)–H(13)	112 (4)	H(24)–N(9)–H(25)	91 (6)
Co(1)–N(5)–H(14)	115 (3)	H(24)–N(9)–H(26)	111 (9)
		H(25)–N(9)–H(26)	104 (8)

the nitrate groups is 1.24 Å, a value slightly higher than expected but not significantly so in view of the relatively higher standard deviations of the atomic positions compared with those of the cation atoms.

Three of the nitrate groups are planar well within experimental error. The nitrate group containing N(13), however, appears to be significantly nonplanar, the nitrogen atom being located about 0.1 Å above the plane of the oxygen atoms. The large thermal vibration amplitudes for the atoms of this group, all nearly 0.4 Å and perpendicular to the plane of the oxygen atoms, and the possibilities for the formation of alternative hydrogen bonds suggest that this nitrate group is either partially disordered or that it is confined in a very wide and shallow potential well which permits it to vibrate freely with such large amplitudes.

Table VIII

Hydrogen-Bonding Scheme

Bonded atoms	N–O distance, Å	Bonded atoms	N–O distance, Å
N(1)–H(1)–O(8)	3.111	N(5)–H(14)–O(8)	2.920
N(1)–H(2)–O(12)[f]	3.284	N(6)–H(15)–O(5)[e]	3.158
N(2)–H(3)–O(13)[c]	3.003	N(6)–H(16)–O(7)	2.991
N(2)–H(4)–O(4)[h]	2.929	N(6)–H(17)–O(9)	3.030
N(2)–H(5)–O(9)[c]	3.003	N(7)–H(18)–O(14)[f]	3.256
N(3)–H(6)–O(6)[g]	3.283	N(7)–H(19)–O(9)	3.368
N(3)–H(7)–O(7)[c]	3.222	N(7)–H(20)–O(6)[b]	3.200
N(3)–H(8)–O(11)[d]	2.966	N(8)–H(21)–O(11)	3.035
N(4)–H(9)–O(12)[c]	3.052	N(8)–H(22)–O(5)[e]	3.137
N(4)–H(10)–O(12)[f]	3.027	N(8)–H(23)–O(14)[b]	3.195
N(4)–H(11)–O(3)[a]	3.089	N(9)–H(24)–O(8)[b]	3.106
N(5)–H(12)–O(6)[g]	2.989	N(9)–H(25)–O(10)[c]	3.289
N(5)–H(13)–O(10)[d]	3.097	N(9)–H(26)–O(5)[h]	2.921

[a–h] Oxygen positions other than the x, y, z in Table II: (a) $x - 1, y, z$; (b) $x + 1, y, z$; (c) $x, {}^1/_2 - y, z - {}^1/_2$; (d) $x - 1, {}^1/_2 - y, z - {}^1/_2$; (e) $x, {}^1/_2 - y, z + {}^1/_2$; (f) $1 - x, y - {}^1/_2, {}^1/_2 - z$; (g) $1 - x, y + {}^1/_2, {}^1/_2 - z$; (h) $2 - x, -y, -z$.

Table IX

Rms Displacements (in Å) Along the Principal Axes of the Temperature Factor Ellipsoids[a]

Atom	Axis 1	Axis 2	Axis 3
Co(1)	0.149 (2)	0.146 (2)	0.124 (2)
Co(2)	0.156 (2)	0.146 (2)	0.129 (2)
O(1)	0.183 (8)	0.157 (6)	0.137 (6)
O(2)	0.204 (7)	0.163 (6)	0.132 (6)
N(1)	0.157 (10)	0.147 (8)	0.124 (8)
N(2)	0.201 (8)	0.180 (7)	0.149 (8)
N(3)	0.231 (8)	0.191 (8)	0.155 (7)
N(4)	0.202 (8)	0.177 (8)	0.160 (8)
N(5)	0.190 (7)	0.155 (8)	0.142 (8)
N(6)	0.220 (7)	0.172 (7)	0.139 (9)
N(7)	0.222 (9)	0.204 (7)	0.149 (8)
N(8)	0.223 (10)	0.186 (7)	0.146 (7)
N(9)	0.210 (7)	0.176 (8)	0.158 (8)
N(10)	0.252 (8)	0.206 (7)	0.176 (9)
O(3)	0.248 (6)	0.238 (7)	0.152 (7)
O(4)	0.408 (8)	0.306 (7)	0.185 (6)
O(5)	0.425 (8)	0.233 (6)	0.182 (7)
N(11)	0.233 (9)	0.180 (9)	0.165 (6)
O(6)	0.386 (7)	0.194 (6)	0.154 (5)
O(7)	0.290 (7)	0.254 (8)	0.196 (6)
O(8)	0.255 (8)	0.222 (6)	0.151 (4)
N(12)	0.224 (9)	0.180 (8)	0.159 (7)
O(9)	0.222 (7)	0.214 (6)	0.186 (7)
O(10)	0.260 (7)	0.250 (6)	0.153 (8)
O(11)	0.283 (6)	0.212 (7)	0.151 (5)
N(13)	0.289 (8)	0.214 (8)	0.145 (11)
O(12)	0.425 (9)	0.271 (8)	0.227 (8)
O(13)	0.331 (8)	0.213 (6)	0.166 (5)
O(14)	0.336 (8)	0.267 (7)	0.230 (7)

[a] Values in parentheses are estimated standard deviations.

The hydrogen positions as obtained from the least-squares refinement are, in general, chemically reasonable. The bond distances and angles involving the hydrogen atoms are given in Tables VI and VII. Although the calculated N–H distances range down to 0.52 Å, the shorter values pertain to those hydrogen atoms having large temperature motions and, concomitantly, large standard deviations in their positions.

The ions appear to be held together in the crystal by a network of hydrogen bonds. The lengths of most of

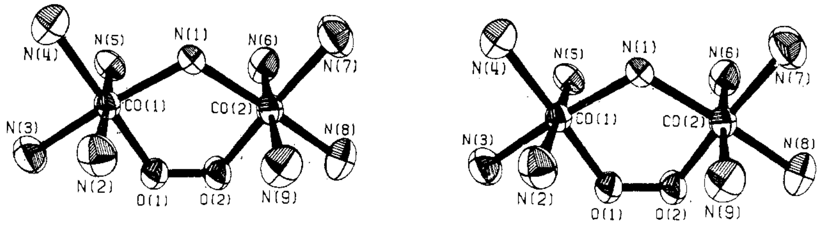

Figure 3.—The thermal motion of the cation. Thermal ellipsoids are drawn at the 0.74 probability level.

the interactions we have characterized as hydrogen bonds are somewhat longer than the average value of 2.88 ± 0.13 Å tabulated by Pimentel and McClellan[21] for bonds of the type $N^+\text{–}H\cdots O$. The crowding between the many acceptor atoms surrounding each cation is perhaps responsible for the hydrogen bonds being longer than normal. Table VIII lists what we consider to be a probable hydrogen-bonding scheme. The oxygen atoms in the superoxo bridge appear to be the only oxygen atoms in the crystal that are not involved in hydrogen bonding. Space-filling atomic models show that these bridge atoms are thoroughly shielded by ammonia groups.

Thermal Vibrations

The thermal vibrations of the atoms in the cation are in general what would be expected from a consideration of its geometry. The vibrations of the cobalt atoms and of the ring nitrogen atom are essentially isotropic with rms amplitudes of roughly 0.15 Å. The superoxo oxygen atoms have somewhat larger excursions perpendicular to the ring plane with rms amplitudes of about 0.20 Å. The rms amplitudes of vibration of the ammine nitrogen atoms are between 0.15 and 0.23 Å with the maximum amplitudes in directions very nearly perpendicular to the Co–N bonds. These thermal motions can best be understood by looking at Figure 3.

The vibrations of the nitrate group atoms are significantly larger than those of the cation atoms, their rms amplitudes ranging from 0.14 to 0.43 Å and averaging about 0.21 Å. The largest vibrations are generally perpendicular to the planes of the ions, particularly in the nitrate group containing N(13). As was discussed previously, it appears as if this whole group is vibrating in a wide, shallow potential well.

No attempt was made to correct the bond lengths for thermal vibration. The rms displacements of the atoms along the principal axes of their thermal ellipsoids are given in Table IX.

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(21) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p 289.