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The Crystal Structure of $K_3[Hg(NO_2)_4]NO_3$

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The compound previously believed to be $K_3[Hg(NO_2)_5]H_2O$ has been shown by crystal structure analysis to be correctly formulated $K_3[Hg(NO_2)_4]NO_3$, containing $[Hg(NO_2)_4]^{2-}$ and nitrate as discrete anions. The nitrite ions are co-ordinated to the mercury through both oxygens, and thus function as bidentate chelates. The configuration of the eight oxygen atoms about the mercury is as the vertices of a severely distorted square antiprism.

Introduction

Pale yellow crystals of a mixed potassium mercury nitrite were prepared in a number of early studies[1-3] by mixing solutions of mercuric nitrate and potassium nitrite, and the crystals were formulated $2KNO_2 . Hg(NO_2)_2$. Rohenheim and Oppenheimer[4] suggested that the nitrite analysis was low due to oxidation of nitrous acid by mercuric oxide and, by an undisclosed procedure, themselves determined that there were five nitrite ions per molecule. From this, and mercury and potassium analysis, they deduced the formula to be $3KNO_2 . Hg(NO_2)_2 . H_2O$. The presence of a molecule of water was re-affirmed by other workers,[5-6] but in no instance was any direct evidence for its existence quoted. Indeed, the failure of an attempt to remove the water by intensive drying led to the supposition that it is co-ordinated to the mercury atom,[5] and that the correct formulation is $K_3[Hg(NO_2)_5 . H_2O]$. It is noteworthy that a more recent attempt[7] to prepare mixed nitrites from solutions of mercuric nitrite and potassium *nitrite* failed to yield the above compound at all.

We have determined the crystal structure of this compound and have thus demonstrated that all of these formulations are incorrect. The crystals do not contain the anion $[Hg(NO_2)_5 . H_2O]^{3-}$ but rather the anion $[Hg(NO_2)_4]^{2-}$ and a discrete nitrate ion, and the correct formula is then $K_3[Hg(NO_2)_4]NO_3$. A preliminary account of this work has previously been published.[8]

(1) J. Lang, *Journ. prakt. Chem.*, *86*, 295 (1862).
(2) C. F. Rammelsburg, Pogg. Annalen, *118*, 249 (1863).
(3) A. Fock, *Zeit. Krist.*, *17*, 188 (1889).
(4) A. Rosenheim and K. Oppenheim, *Zeit anorg. Chem.*, *28*, 171, (1901).
(5) V. Kohlschutter, *Ber.*, *35*, 489 (1902).
(6) P. C. Ray, *J. Chem. Soc.*, *91*, 2031 (1907).
(7) A. Ferrari and C. Colla, *Gazz. Chim. Ital.*, *65*, 789 (1935).
(8) D. Hall and R. V. Holland, *Proc. Chem. Soc.*, 204, (1963).

Experimental

Crystals of $K_3HgN_5O_{11}$ were prepared as described above, and recrystallised from water as small yellow prisms. Analysis (by Dr. A.D. Campbell of the University of Otago) gave: Found: K=21.4, total N = 12.4%; Calculated, K= 20.8, N = 12.0%. After the structure had indicated the existence of separate nitrite and nitrate groupings an iodometric titration for nitrite gave: Found, 32.6; Calculated for 4 nitrite ions per mercury atom 32.6%. Analyses in an independent study[9] confirm the difference between nitrite and total nitrogen content.

The crystals were established as orthorhombic, and unit cell dimensions were measured from rotation photographs, taken with CuKα radiation, as $a=12.12\pm.04$, $b=10.58\pm.03$, $c=9.28\pm.03$ Å. The errors quoted represent the range of individual measurements. The density measured by displacement of bromoform was 3.0 ± 0.1 gr. cm^{-3}, the density calculated for 4 molecules per unit cell is 3.14 gr. cm^{-3}. Reflections were systematically absent for hk0 with k odd, 0kl with k+1 odd, and the space group is then Pnma, or Pn2_1a. The crystals gave a negative pyrolectric test, which supports the subsequent deduction that Pnma is correct.

Intensity data were measured visually from Weissenberg photographs, taken with nickel-filtered CuKα radiation, of the layers h0l—h4l and 0kl—3kl. The crystals used were of square cross-section, with maximum dimension 0.008 cm^{-1}. The linear absorption coefficient is 3.3×10^2 cm^{-1}. Cylindrical absorption corrections were applied, as well as the usual Lorentz and polarisation corrections. The final data set comprised 976 non-zero reflections.

The mercury atom was located from Patterson projections, and the potassium ions from electron density projections. It was apparent that their arrangement was consistent with space group Pnma, with the mercury and one potassium on the mirror plane at $y=1/4$. A three dimensional difference density synthesis, assuming Pnma, revealed all of the light atoms with peak heights all greater than 6 e Å^{-3}, whereas the background never exceeded 2 e Å^{-3}, and as the structure was sensible and immediately interpretable the centrosymmetric space group was not thereafter questioned. Refinement proceeded by block-diagonal least squares, assuming anisotropic thermal motion for the mercury and potassium atoms, and isotropic

(9) J. I. Bullock and D. G. Tuck, *J. Chem. Soc.*, 1877, (1965).

Table I. Atom Coordinates

Atom	x/a	y/b	z/c
Hg	.0923	.25	.1879
K(1)	.0176	.25	.6021
K(2)	.3017	.0046	.4384
N(1)	.0406	.0036	.2959
N(2)	.3413	.25	.1496
N(3)	−.0299	.25	−.0881
N(4)	.2492	.25	.7370
O(1)	.0211	.0296	.1702
O(2)	.0776	.0851	.3729
O(3)	.2812	.1521	.1725
O(4)	−.0816	.25	.0282
O(5)	.0760	.25	−.0638
O(6)	.2232	.1496	.6753
O(7)	.2980	.25	.8618

motion for the light atoms, to an R index $(\Sigma\,|\,F_o\,|\,/\Sigma\,|\,F_o{-}F_c\,|\,)$ of .154 for the 976 observed data. Scattering factors were as in the International Tables,[10] with a real dispersion correction for mercury. The weight function was $w=1/(1+(\,|\,F_o\,|-b)^2/a^2)$, with a and b chosen such that mean $w\Delta^2$ was approximately constant over the range of $|\,F_o\,|$.

Observed and calculated structure factors are listed in Table II. The dimensions of the anions are listed in Tables III and IV, and the closer approaches to the potassium ions in Table V. Standard deviations in these quantities are somewhat variable, but as they are high, and thus individually unlikely to be the subject of detailed argument, the ranges only for different types of bond and angle are listed in Table VI.

Table II. Observed and Calculated Structure Factors.

L	FO	FC
H= 0, K= 0		
4	542	-1177
6	1530	-2174
10	735	717
12	56	28
H= 0, K= 1		
5	1167	1076
7	2655	-2679
9	1121	967
11	485	-401
H= 0, K= 2		
2	1642	1513
4	541	386
6	1282	-1288
8	232	757
10	1031	-1130
H= 0, K= 3		
3	1841	-1836
5	654	-669
7	1667	1557
9	568	-1071
11	384	391
H= 0, K= 4		
0	4926	4594
2	692	-733
4	337	-55
6	245	334
8	1563	-1785
10	667	726
H= 0, K= 5		
1	2020	-1941
3	1282	1160
H= 0, K= 6		
0	1653	-1515
2	1141	1160
H= 0, K= 7		
1	1460	1084
3	1135	-1028
H= 0, K= 8		
0	2727	3336
2	506	-825
H= 0, K= 9		
1	1461	-1150
3	957	832
H= 0, K= 10		
0	1477	-1449
2	789	1161
H= 0, K= 11		
1	1216	768
3	842	-698
H= 0, K= 12		
0	1517	2075
2	449	-563
H= 0, K= 13		
1	1006	-893
H= 1, K= 0		
3	725	-403
6	470	-414
7	748	-782
9	1001	-1004
10	557	456
11	700	763
H= 1, K= 1		
1	684	-644
2	1456	-1687
3	1376	1533
4	1680	1838
5	1116	-574
6	1218	-1057
7	263	207
8	350	145
9	655	402
10	667	593
11	636	-497
H= 1, K= 2		
1	700	-532
2	1568	2099
3	1366	1404
4	604	-753
5	1802	-1986
6	1261	1202
7	736	668
8	232	-85
9	217	264
10	694	-696
11	613	-656
H= 1, K= 3		
1	570	513
2	1759	1680
3	1655	-1539
4	1354	-1579
5	712	797
6	760	664
7	350	-190
8	345	-205
9	314	-374
10	260	-366
11	728	434
H= 1, K= 4		
1	1292	1295
2	345	200
3	1333	-1365
4	1642	1526
5	1325	1531
6	248	-49
7	628	-518
8	243	215
9	781	-849
10	171	58
11	475	652
H= 1, K= 5		
1	488	-400
2	1524	-1568
3	1317	1259
H= 1, K= 6		
1	306	-257
2	740	742
3	1263	1150
H= 1, K= 7		
1	1466	452
2	952	914
3	881	-862
H= 1, K= 8		
1	952	653
2	508	-345
3	845	-812
H= 1, K= 9		
1	345	-287
2	1376	-1273
3	940	904
H= 1, K= 10		
1	329	-351
2	1165	1021
H= 1, K= 11		
1	346	363
2	837	674
3	613	-550
H= 1, K= 12		
1	551	279
2	209	-203
3	191	-416
H= 1, K= 13		
1	158	-119
2	562	-645
H= 2, K= 0		
0	876	930
2	618	-727
6	475	376
7	1044	-1025
8	250	-155
9	1162	1047
10	1098	964
11	692	-668
H= 2, K= 1		
0	2375	-2459
1	968	-1030
2	1575	1718
3	1208	1197
4	214	102
5	541	395
6	962	-950
7	1098	-855
8	1593	1353
9	245	192
10	1165	-856
11	153	-99
H= 2, K= 2		
0	1297	-1302
1	1808	1738
2	2302	-1331
3	590	-537
4	332	125
5	269	-217
6	717	584
7	1258	1354
8	991	645
9	1325	-1218
10	447	-351
11	248	146
H= 2, K= 3		
0	1348	1632
1	454	338
2	1453	-1454
3	1136	-1138
4	296	314
6	705	824
7	825	817
8	1111	-1510
9	309	-227
10	671	825
H= 2, K= 4		
0	1616	1696
1	1917	-1676
2	1363	-1292
3	1021	1681
4	452	-351
5	1098	1163
6	786	898
7	1108	-1267
8	587	-574
9	950	1130
10	881	886
11	396	-524
H= 2, K= 5		
0	1686	-1958
1	1088	-916
2	1299	1450
3	965	942
H= 2, K= 6		
0	1897	-2000
1	1649	1879
2	294	-270
3	899	-278
H= 2, K= 7		
0	1478	1659
1	479	435
2	1100	-1044
3	608	-551
H= 2, K= 8		
0	651	530
1	1315	-1179
2	603	-537
3	1037	1047
H= 2, K= 9		
0	1054	-1139
1	768	-539
2	1105	1019
3	883	742
H= 2, K= 10		
0	904	-716
1	1264	577
2	296	-283
3	295	-324
H= 2, K= 11		
0	955	1098
1	266	310
2	791	-684
3	518	-339
H= 2, K= 12		
0	281	383
1	1024	-854
2	434	-314
3	186	582
H= 2, K= 13		
0	725	-837
1	373	-342
2	536	666
H= 3, K= 0		
1	786	-773
2	1070	-1246
3	863	-679
4	1134	1178
5	508	360
6	1154	-1165
7	955	886
8	248	159
9	230	-69
10	1059	963
11	138	-72
H= 3, K= 1		
1	536	-504
2	202	-97
3	1999	2006
4	580	-366
5	2022	-2052
6	544	397
7	1006	895
8	263	125
9	753	621
10	636	-159
11	980	-897
H= 3, K= 2		
1	761	-669
2	1425	1447
3	600	-566
4	2635	-2634
5	214	209
6	728	606
7	406	330
8	230	-305
9	534	332
10	671	-525
11	498	455
H= 3, K= 3		
1	929	810
3	2216	-2169
4	306	594
5	1254	1643
6	345	-361
7	702	-633
8	342	-200
9	567	-419
10	243	209
11	812	751
H= 3, K= 4		
1	1228	-962
2	2604	-2509
3	209	135
4	1810	1877
5	240	-56
6	883	-926
7	659	725
8	235	-103
9	207	143
10	809	996
11	94	-197
H= 3, K= 5		
1	694	-566
2	281	-102
3	1716	1683
H= 3, K= 6		
1	317	-247
2	1047	1209
3	661	-614
H= 3, K= 7		
1	472	313
2	314	-100
3	1305	-1391
H= 3, K= 8		
1	807	-561
2	1202	-1311
H= 3, K= 9		
1	871	-624
2	317	-52
3	1445	1368
H= 3, K= 10		
1	319	-279
2	802	774
3	261	-77
H= 3, K= 11		
1	278	248
3	1006	-998
H= 3, K= 12		
1	546	-374
2	735	-694
3	176	155
H= 3, K= 13		
1	311	-305
H= 4, K= 0		
0	442	367
2	605	551
3	217	226
4	536	-385
5	582	489
6	917	-874
7	1562	-1567
8	766	663
9	1310	1148
10	523	-390
H= 4, K= 1		
0	2916	-2658
1	2175	2291
2	1407	1368
3	232	-138
4	697	587
5	618	-497
6	973	-853
7	883	633
8	1014	944
9	235	-808
10	720	-561
11	393	375
H= 4, K= 2		
0	1621	1615
1	469	570
2	1190	-1046
3	1853	-1743
4	426	348
5	1351	-1176
6	1379	1201
7	985	816
8	1149	-1334
9	842	-724
10	398	301
11	531	396
H= 4, K= 3		
0	1562	1549
1	2040	-2112
2	1238	-1225
3	260	242
4	319	-91
5	334	452
6	725	750
7	595	-743
9	712	826
10	585	600
11	140	-296
H= 4, K= 4		
0	771	-714
1	1652	-1509
2	1238	1079
3	380	408
4	442	-216
5	245	-183
6	1151	-1273
7	1174	-1200
8	924	948
9	1019	1076
10	317	-349
11	69	-36
H= 4, K= 5		
0	1892	-2168
1	1621	1542
2	1105	1089
3	296	-248
H= 4, K= 6		
0	1437	1672
1	687	573
2	919	-998
3	1026	-1011
H= 4, K= 7		
0	1172	1341
1	1779	-1653
2	797	-915
3	319	134
H= 4, K= 8		
0	414	-440
2	717	683
3	317	315
H= 4, K= 9		
0	1289	-1296
1	1307	1006
2	763	725
3	304	-210
H= 4, K= 10		
0	753	588
1	894	641
2	603	-457
3	878	-798
H= 4, K= 11		
0	722	838
1	1343	-1052
2	202	-643
3	222	115
H= 4, K= 12		
0	250	-426
1	1085	-900
2	539	479
3	158	155
H= 4, K= 13		
0	842	-970
H= 4, K= 10		
1	500	641
H= 5, K= 0		
1	654	-606
2	766	-675
4	756	630
5	1864	-1959
6	500	-217
7	503	212
8	240	81
9	212	27
10	485	392
11	927	-1128
H= 5, K= 1		
1	365	278
2	988	898
3	227	183
4	1958	-2051
5	638	-596
6	1461	1470
7	266	217
8	253	168
9	475	285
10	883	-742
11	255	-192
H= 5, K= 2		
1	2563	2678
2	633	628
3	2070	-2051
4	682	-617
5	1294	1192
6	437	266
7	1136	-880
8	551	-432
9	1047	-820
10	161	-95
11	674	796
H= 5, K= 3		
1	406	-45
2	1345	-1398
3	393	-322
4	1619	1993
5	595	424
6	1164	-1265
7	345	-139
8	322	-228
9	276	-177
10	534	731
11	100	126
H= 5, K= 4		
1	483	-435
2	311	-316
3	1700	1759
4	240	66
5	1136	-1258
6	250	64
7	243	149
8	220	224
9	184	-243
10	135	107
H= 5, K= 5		
1	319	96
2	562	619
3	304	318
H= 5, K= 6		
1	1399	1456
2	314	96
3	973	-1027
H= 5, K= 7		
1	345	-167
2	753	-913
3	319	-84
H= 5, K= 8		
1	730	-503
2	319	-342
3	1736	1625
H= 5, K= 9		
1	329	-30
2	304	625
3	294	280
H= 5, K= 10		
1	1468	1137
2	392	468
3	1208	-1092
H= 5, K= 11		
1	248	-72
2	740	-688
3	207	-97
H= 5, K= 12		
1	181	-307
2	158	-120
3	886	1061
H= 6, K= 0		
1	1082	927
2	1534	1649
3	728	581
4	355	-360
5	523	299
6	1305	-1300
7	776	632
8	1210	1082
9	751	-508
10	646	-631
11	220	-169
H= 6, K= 1		
0	694	598
2	625	-490
3	240	-243
4	250	78
5	753	-474
6	654	459
7	1287	1038
8	597	-476
9	1305	-1104
10	158	131
11	401	621
H= 6, K= 2		
0	2778	2392
1	1031	-954
2	1223	-1288
3	1024	969
4	613	594
5	1044	851
6	1210	1595
7	562	-359
8	1792	-1611
9	544	432
10	521	435
H= 6, K= 3		
0	766	-737
1	1645	-1692
2	722	626
3	294	494
5	350	513
6	350	-565
7	1067	-1223
8	306	436
9	1072	1201
10	184	-161
H= 6, K= 4		
0	942	-979
1	227	190
2	1108	1238
3	760	615
4	740	-697
5	756	560
6	583	-966
7	235	198
8	743	1044
9	168	-338
10	500	-605
H= 6, K= 5		
0	396	435
1	1527	1566
2	211	-295
3	314	-285
H= 6, K= 6		
0	1506	1856
1	342	-264
2	817	-909
3	766	693
H= 6, K= 7		
0	587	-458
1	1566	-1557
2	322	533
3	317	215
H= 6, K= 8		
0	1003	-1063
1	729	520
2	543	1071
3	306	353
H= 6, K= 9		
0	386	374
1	1425	553
2	251	-167
3	278	-335
H= 6, K= 10		
0	1690	1205
1	656	-562
2	812	-737
3	555	404
H= 6, K= 11		
0	276	-292
1	1238	-1015
2	439	387
3	164	163
H= 6, K= 12		
0	779	-883
1	442	357
2	562	750
3	69	189
H= 7, K= 0		
1	1155	-551
2	1145	1056
3	268	-55
4	1287	-1373
5	518	-402
6	1516	1455
7	1029	932
9	488	315
10	669	-662
H= 8, K= 1		
10	603	576
H= 7, K= 1		
1	743	744
2	641	578
3	1310	-1260
4	1245	-1272
5	883	645
6	1019	812
7	657	-585
8	472	216
9	403	-201
10	457	-363
H= 7, K= 2		
1	555	446
2	546	-475
3	1228	-1275
4	2632	2041
5	1052	685
6	745	-593
7	222	-96
8	434	-274
9	161	117
10	437	477
H= 7, K= 3		
1	733	-616
2	650	-940
3	1407	1402
4	1374	1346
5	632	-654
6	345	-528
7	324	454
8	283	-256
9	227	227
10	148	152
H= 7, K= 4		
1	1460	-1430
2	883	902
3	1053	940
4	1082	-1114
5	634	-557
6	1131	1228
7	728	621
8	191	-56
9	569	468
10	342	-532
H= 7, K= 5		
1	679	657
2	597	507
3	1034	-1083
H= 7, K= 6		
1	516	325
2	322	-210
3	1187	-1148
H= 7, K= 7		
1	641	-561
2	319	-489
3	1208	1142
H= 7, K= 8		
1	1001	-863
2	740	815
3	291	521
H= 7, K= 9		
1	687	511
2	684	560
3	756	-750
H= 7, K= 10		
1	255	175
2	230	-261
3	641	-575
H= 7, K= 11		
1	465	-357
2	174	-330
3	740	773
H= 7, K= 12		
1	449	-488
H= 8, K= 0		
0	914	-786
1	1108	1135
2	567	-457
3	717	-597
5	1001	-852
6	245	100
7	677	477
8	585	440
9	749	-730
10	294	214
H= 8, K= 1		
0	1596	1715
1	518	384
2	1422	-1371
3	311	34
4	421	67
5	266	39
6	1067	1031
7	240	-105
8	1445	-1301
9	166	-97
H= 8, K= 2		
0	830	-618
1	2267	-2186
2	227	-346
3	401	409
4	235	60
5	661	559
6	227	600
7	1386	-1150
8	181	135
9	1210	1127
10	79	77
H= 8, K= 3		
0	1391	-1553
1	337	-162
2	1254	1331
8	1305	1403
5	194	145
H= 8, K= 4		
0	725	-548
1	1453	1562
2	250	-326
3	524	-750
4	250	-177
5	1228	-1042
7	1068	653
8	605	540
9	712	-650
H= 8, K= 5		
0	1225	1305
1	345	226
2	1090	-1131
3	319	78
H= 8, K= 6		
0	414	-305
1	2619	-2104
2	319	-277
3	314	251
H= 8, K= 7		
0	1565	-1541
1	334	-270
2	1065	1075
3	296	40
H= 8, K= 8		
0	378	-392
1	1164	1041
2	283	-205
3	664	-518
H= 8, K= 9		
0	886	856
1	274	143
2	835	-858
H= 8, K= 10		
0	278	-390
1	1151	-1067
2	202	-135
3	164	258
H= 8, K= 11		
0	878	-1077
1	682	-174
2	623	740
3	105	55
H= 9, K= 0		
1	296	201
2	286	-205
3	549	-546
4	2173	-2125
5	917	714
6	955	826
7	365	-268
H= 9, K= 1		
1	640	615
2	1054	-942
3	1468	-1464
4	786	677
5	1057	872
6	577	-337
7	837	-623
H= 9, K= 2		
1	232	133
2	942	-1023
3	565	515
4	868	1075
5	227	-662
6	1233	-1115
H= 9, K= 3		
1	1085	-1643
2	865	732
3	1529	1600
4	345	-597
5	334	-724
6	334	335
H= 9, K= 4		
1	643	388
2	250	115
3	988	-943
4	2063	-1939
5	1067	970
6	569	610
7	181	-224
H= 9, K= 5		
1	728	580
2	812	-829
3	1236	-1168
H= 9, K= 6		
1	334	-115
2	309	-593
3	814	765
H= 9, K= 7		
1	996	-735
2	288	617
3	1141	1157
H= 9, K= 8		
1	286	178
2	258	207
3	531	-498
H= 9, K= 9		
1	597	499
2	577	-599
3	988	-1010
H= 9, K= 10		
1	189	52
2	574	-527
3	268	284
H= 10, K= 0		
0	2305	2109
1	973	866
2	562	-372
3	250	-174
4	245	-236
5	730	-534
6	702	524
7	454	231
8	1154	-1265
9	380	-414
H= 10, K= 1		
0	521	553
1	1305	-1249
2	638	-537
3	761	709
4	258	101
5	245	293
6	618	382
7	1271	-1017
8	631	-589
9	656	751
H= 10, K= 2		
0	1128	-1032
1	1162	-997
2	1243	1293
3	401	304
4	225	82
5	212	370
6	1067	-1028
7	508	-445
8	610	653
H= 10, K= 3		
0	347	-445
1	1185	1096
2	751	593
3	899	-756
4	329	-246
5	309	-271
6	419	-450
7	917	940
8	603	743
H= 10, K= 4		
0	1754	1725
1	248	243
2	245	-266
3	100	-235
4	227	-142
5	212	-130
6	467	406
7	153	55
8	848	-1145
H= 10, K= 5		
0	398	421
1	1185	-1075
2	304	-445
3	684	560
H= 10, K= 6		
0	929	-870
1	855	-673
2	1126	1045
3	273	109
H= 10, K= 7		
0	820	-578
1	1062	899
2	536	504
3	613	-633
H= 10, K= 8		
0	1310	1333
1	546	456
2	225	-269
3	209	-159
H= 10, K= 9		
0	250	155
1	691	-845
2	179	-300
3	375	402
H= 10, K= 10		
0	544	-723
1	587	-580
H= 11, K= 0		
1	911	839
2	518	-295
3	1371	-1367
4	523	386
5	1463	1514
6	460	340
7	684	-643
H= 11, K= 1		
1	304	157
2	1052	-1075
3	250	114
4	1220	1212
5	610	-415
6	1039	-837
7	163	-113
8	115	60
H= 11, K= 2		
1	227	-343
2	225	525
3	1136	1214
4	209	635
6	168	336
7	138	126
8	268	-229
H= 11, K= 3		
1	329	[illegible]
2	1445	1141
3	294	132
4	1190	-1195
5	276	405
6	722	721
H= 11, K= 4		
1	784	665
2	227	42
3	1031	-1010
4	204	176
5	1169	1139
6	156	240
7	467	-586
H= 11, K= 5		
1	304	174
2	1024	-1005
3	263	135
H= 11, K= 6		
1	281	-141
2	255	523
3	705	793
H= 11, K= 7		
1	250	-106
2	809	812
3	207	78
H= 11, K= 8		
1	623	580
3	715	-952
H= 11, K= 9		
1	151	203
2	590	-619
3	84	86
H= 12, K= 0		
0	840	768
1	1057	-837
2	848	-759
3	891	780
5	842	669
6	700	593
7	865	-889
H= 12, K= 1		
0	973	-990
1	980	-977
2	620	547
3	227	319
4	212	162
5	572	487
6	454	-407
7	637	-778
H= 12, K= 2		
0	1529	-1623
1	894	772
2	587	537
3	590	-125
4	378	-223
5	163	15
6	135	-321
H= 12, K= 3		
0	1200	997
1	919	877
2	674	-485
3	260	-370
4	260	-188
5	230	-357
6	186	343
H= 12, K= 4		
0	720	769
1	919	-531
2	932	-806
3	897	630
4	174	60
5	454	469
6	615	675
H= 12, K= 5		
0	1024	-968
1	952	-862
2	587	569
3	225	315
H= 12, K= 6		
0	1542	-1603
1	574	523
2	500	543
3	194	-134
H= 12, K= 7		
0	720	739
1	890	835
2	375	-360
3	156	-207
H= 12, K= 8		
0	419	552
1	493	-491
2	403	-587
3	314	506
H= 13, K= 0		
1	554	-275
2	1320	-1251
3	314	-284
4	789	793
5	661	581
6	498	-657
H= 13, K= 1		
1	214	-192
2	253	-164
3	942	939
4	439	302
5	1210	-1160
6	421	-339
H= 13, K= 2		
1	666	-502
2	876	850
3	166	58
4	929	-1004
5	125	-111
6	666	358
H= 13, K= 3		
1	260	136
2	232	319
3	894	-865
5	663	1087
6	105	225
H= 13, K= 4		
1	174	-51
2	1231	-1305
3	498	-558
4	674	893
5	424	585
H= 13, K= 5		
1	217	-242
2	191	-112
3	802	904
H= 13, K= 6		
1	467	-380
2	702	858
3	135	57
H= 13, K= 7		
2	105	177
H= 14, K= 0		
0	232	-138
1	1019	-935
2	500	370
3	340	252
4	125	-123
5	89	37
H= 14, K= 1		
0	1274	-1541
1	227	182
2	781	743
3	151	-72
4	329	198
5	89	-117
H= 14, K= 2		
0	151	199
1	628	579
2	140	-124
3	802	-1002
5	202	-507
H= 14, K= 3		
0	975	1090
1	421	-236
2	643	-693
3	161	-19
4	135	-102
H= 14, K= 4		
0	516	-447
1	715	-931
2	429	460
3	105	297
4	64	34
H= 14, K= 5		
0	934	-1226
1	151	191
2	452	634
3	82	-77
H= 14, K= 6		
0	112	212
H= 15, K= 0		
1	143	40
2	646	-829
3	551	757
H= 15, K= 1		
1	161	-77
2	442	507
3	375	592
H= 15, K= 2		
1	355	590
2	447	544
3	191	-540

Table III. Dimensions of the $[Hg(NO_2)_4]^{2-}$ ion (Distances in Å, angles in degrees).

O(1)—N(1)	1.22	O(1)—N(1)—O(2)	118.5
O(2)—N(1)	1.21		
O(3)—N(2)	1.28	O(3)—N(2)—O(3)′	107.5
O(4)—N(3)	1.25	O(4)—N(3)—O(5)	110.2
O(5)—N(3)	1.30		
Hg—O(1)	2.49	Hg—N(1)	2.86
Hg—O(2)	2.45	Hg—N(2)	3.04
Hg—O(3)	2.52	Hg—N(3)	2.96
Hg—O(4)	2.58		
Hg—O(5)	2.34		
Hg—O(1)—N(1)	94.6	Hg—O(2)—N(1)	97.0
Hg—O(3)—N(2)	101.2		
Hg—O(4)—N(3)	94.9	Hg—O(5)—N(3)	104.9
O(1)—O(2)	2.09	O(1)—Hg—O(2)	49.9
O(1)—O(1)′	4.66	O(1)—Hg—O(1)′	138.7
O(1)—O(2)′	4.54	O(1)—Hg—O(2)′	133.4
O(1)—O(3)	3.41	O(1)—Hg—O(3)	85.8
O(1)—O(3)′	4.61	O(1)—Hg—O(3)′	134.1
O(1)—O(4)	2.95	O(1)—Hg—O(4)	71.3
O(1)—O(5)	3.26	O(1)—Hg—O(5)	84.6
O(2)—O(1)	2.09	O(2)—Hg—O(1)	49.9
O(2)—O(1)′	4.54	O(2)—Hg—O(1)′	133.4
O(2)—O(2)′	3.49	O(2)—Hg—O(2)′	90.7
O(2)—O(3)	3.17	O(2)—Hg—O(3)	79.2
O(2)—O(3)′	4.16	O(2)—Hg—O(3)′	113.4
O(2)—O(4)	4.12	O(2)—Hg—O(4)	110.1
O(2)—O(5)	4.41	O(2)—Hg—O(5)	133.7
O(3)—O(3)′	2.08	O(3)—Hg—O(3)′	48.6
O(3)—O(1)′	3.41	O(3)—Hg—O(1)	85.8
O(3)—O(2)	3.17	O(3)—Hg—O(2)	79.2
O(3)—O(1)′	4.61	O(3)—Hg—O(1)′	134.1
O(3)—O(4)	4.71	O(3)—Hg—O(4)	135.4
O(3)—O(5)	3.47	O(3)—Hg—O(5)	91.1
O(4)—O(5)	2.09	O(4)—Hg—O(5)	50.1
O(4)—O(1) ≡O(4)—O(1)′	2.95	O(4)—Hg—O(1)	71.3
O(4)—O(2) ≡O(4)—O(2)′	4.12	O(4)—Hg—O(2)	110.1
O(4)—O(3) ≡O(4)—O(3)′	4.71	O(4)—Hg—O(3)	135.4
O(5)—O(4)	2.09	O(5)—Hg—O(4)	50.1
O(5)—O(1) ≡O(5)—O(1)′	3.26	O(5)—Hg—O(1)	84.6
O(5)—O(2) ≡O(5)—O(2)′	4.41	O(5)—Hg—O(2)	133.7
O(5)—O(3) ≡O(5)—O(3)′	3.47	O(5)—Hg—O(3)	91.1
N(1)—Hg—N(1)′	131.3	N(1)—Hg—N(2)	104.9
N(1)—Hg—N(3)	101.2	N(2)—Hg—N(3)	113.2

Table IV. Dimensions of the nitrate ion (Distances in Å, angles in degrees).

O(6)—N(4)	1.25	O(6)—N(4)—O(6)′	116.7
O(7)—N(4)	1.30	O(6)—N(4)—O(7)	121.6
O(6)—O(7)	2.22		
O(6)—O(6)′	2.13		

Discussion

The arrangement of nitrogen and oxygen atoms about the mercury atom is shown in Figure 1, and the dimensions of this complex ion are listed in Table III. Note that the mercury atom itself and the

Table V. Close approaches to the potassium ions.

K(1)—O)7) [b]	2.68 Å	K(2)—O(6) [a]	2.84 Å
O(6) [a]	2.79	O(1) [f]	2.86
O(2) [a]	2.85	O(2) [a]	2.91
N(1) [c]	2.93	O(3) [g]	2.91
N(3) [d]	2.93	O(3) [a]	2.93
N(4) [a]	3.07	O(6) [h]	2.95
N(2) [e]	3.17	O(4) [f]	2.97
O(5) [a]	3.18	O(7) [h]	3.04
N(4) [b]	3.58	O(1) [f]	3.06
		O(5) [g]	3.08
Hg [a]	3.95	N(4) [h]	3.34
		Hg [h]	3.78

[a] = x, y, z as in Table I. [b] = ½+x, y, 1−z. [c] = −x, −y, 1−z. [d] = x, y, 1+z. [e] = −½+x, y, ½−z. [f] = ½+x, y, ½−z. [g] = ½−x, y, ½+z. [h] = ½−x, y, −½+z.

Table VI. Range of standard deviations.

Distance	(Å)	Angle	(°)
Hg—K	.009—.011	Hg—O—N	2.0—2.8
Hg—O,N	.027—.039	O,N—Hg—O,N	0.5—1.4
K—O,N	.018—.045	O—N—O	2.0—3.9
O,N—O,N	.018—.058		

atoms O(4), O(5), N(2), and N(3), are situated in the mirror plane. Atoms O(1), O(2), O(3), and N(1) are not, and thus by the reflection operation there are eight oxygen and four nitrogen atoms. These constitute four clearly defined nitrite ions, viz. O(1) — N(1) — O(2) and its reflected image, O(1)′ — N(1)′ — O(2)′; O(3) — N(2) — O(3)′, which thus sits across the mirror plane; and O(4) — N(3) — O(5), which lies in the mirror plane. The nitrogen-oxygen bond lengths range from 1.21 to 1.30 Å, and the oxygen-nitrogen-oxygen angle from 107.5 to 118.5°. In sodium nitrite,[11] the corresponding dimensions are N–O = 1.23±.04 Å, O–N–O = 115.7±3.0 Å.

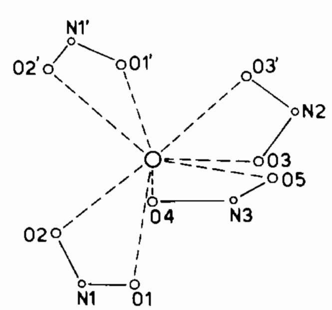

Figure 1. The $[Hg(NO_2)_4]^{2-}$ ion.

The four nitrite groups are disposed such that each is a bidentate ligand, co-ordinated to the mercury through the oxygen atoms. The five independent mercury-oxygen distances range from 2.34 to 2.58 Å whereas the mercury-nitrogen distances are from 2.86 to 2.96 Å. Nitrite has not previously been observed

(10) «International Tables for X-ray Crystallography», Volume 3, Kynock Press, Birmingham, pp. 202-216 (1962).
(11) G. B. Carpenter, *Acta Cryst.*, 5, 132 (1952).

to be bidentate, although it is equally able to span two co-ordination sites as is *e.g.* nitrate[12-13] or carbonate.[14]

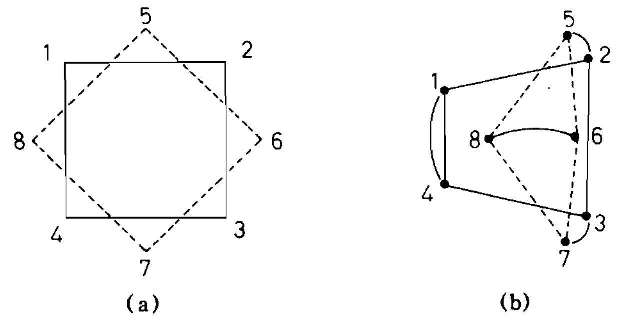

Figure 2. The relationship of the oxygen arrangement to a square antiprism.

The arrangement of the eight ligand oxygens may be considered as being derived from a square antiprism. Using the numbering system[15] for the vertices of the antiprism as in Figure 2a, the mirror plane may be thought of as perpendicular to the paper and containing the line 6-8. The nitrite chelates then span positions 2-5 and the symmetry related 3-7, (O(1) - N(1) - O(2)), 1-4 (O(3) - N(2) - O(3)′) and 6-8 (O(4) - N(3) - O(5)). The distortion arises because the dimensions of the nitrite ion necessitate that these four edges of the polyhedron are much shorter than any other. The square face 1234 of the idealised antiprism thus becomes a trapezium with side 1-4 (at 2.08 Å) shorter than the other three (3.17 to 3.49 Å). More severely, the necessity to compress the diagonal 6-8 of face 5678 means that these four vertices are no longer coplanar and are barely recognisable as having derived from a square (Figure 2b). Indeed, in the classic discussion of Hoard and Silverton[16] of the possible stereoisomers of a tetrakis-bidentate molecule in the square antiprismatic configuration, it was assumed that such bridging could not occur, and thus the presently observed configuration was not a considered possibility. Whether it is still meaningful to use the antiprism as the basis of description after such distortion is debatable, and it may be rather more important to note that the nitrogen-mercury-nitrogen angles are all near tetrahedral. In this respect the configuration complies with the principle enunciated by Cotton and Bergman,[12] *viz.* that a polyatomic ligand, in which two chemically equivalent atoms are held much closer together than such a pair of atoms would be if independent of each other, has a tendency to interact through both of the equivalent atoms in such a way that the mean positions of the pairs of atoms are roughly at the vertices of one of the usual co-ordination polyhedra. The nitrogen atoms in the $[Co(NO_3)_4]^{2-}$ ion[12] and in $Ti(NO_3)_4$,[13] and the bond centres in K_3CrO_8,[17] are thus also tetrahedrally disposed about the central metal, although in each of these instances the ligands are so arranged that the oxygens form a dodecahedron, of D_{2d} symmetry. The configuration observed in $[Hg(NO_2)_4]^{2-}$ has not previously been observed, but reference to Table III demonstrates that it does imply a more or less equivalent environment for all eight oxygens, and thus it should be reasonably effective in minimising internal repulsion. It does then seem a reasonable alternative to the dodecahedron, and further structural work will presumably establish whether it occurs in the present instance because it is more favourable energetically for such a complex for a larger central metal, or whether it is peculiar to the present species, or whether it owes its existence simply to the balance of packing forces in the present structure.

The atoms O(6), O(6)′, O(7), and N(4) exist in the structure as a distinct grouping. These four atoms are coplanar (maximum deviation of .01 Å from the mean plane) with the nitrogen atom at the centre of the three oxygens, and the dimensions of the ion are as in Table IV. This is obviously a nitrate ion - the corresponding dimensions in sodium nitrate[18] are N–O = 1.218±.004 Å, O–N–O = 120°. The closest approach of any of these atoms to the mercury is that of O(7), 3.92 Å, and thus the nitrate is not co-ordinated but exists as a discrete ion. The presence of the nitrate ion has been confirmed by the infra-red spectrum.[9]

The closer approaches of the potassium ions are listed in Table V. Allowing for the fact that K(1) lies in the mirror plane, and thus all of its approaches to atoms not in the plane are duplicated, each potassium can be seen to have ten or eleven oxygen or nitrogen neighbours at distances ranging from 2.68 to 3.2 Å. These form no particular polyhedron but in each case define a more or less spherical cavity in which the potassium ion residues.

There was no sign of any further atom on a difference density synthesis, nor is there any room for a water molecule in the structure. The nitrate ion is independent of the mercury complex and the crystals are in fact a mixed potassium salt of the complex anion and nitrate, with formula $K_3[Hg(NO_2)_4]NO_3$. This does, of course, give virtually the same analysis for potassium, mercury and total nitrogen as the previously supposed formula, and if it is assumed that Rosenheim and Oppenheimer[4] and subsequent workers[5-6] did in fact determine total nitrogen their confusion can be understood. It is also now obvious why the attempt at preparation using potassium nitrite and mercuric nitrite, rather than mercuric nitrate, was not successful.

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(16) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, *2*, 235, (1963).
(17) J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, *37*, 17 (1962).
(18) R. L. Sass, R. Vidale and J. Donohue, *Acta Cryst.*, *10*, 567 (1957).