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The Crystal and Molecular Structure of Nitropentamminocobalt(III) Bromide

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The crystal and molecular structure of nitropentamminocobalt(III) bromide, $[Co(NH_3)_5NO_2]Br_2$, has been solved in order to determine the existence or non-existence of a structural *trans* effect. The crystals are monoclinic (space group $C2/c$, no. 15) with $a=10{\cdot}71$, $b=8{\cdot}791$, $c=11{\cdot}01$ Å and $\beta=94{\cdot}67°$, with four molecules, each possessing a crystallographic twofold axis, per cell. No significant variation among the five cobalt to ammine nitrogen distances is observed; the other general features of the structure are those expected for the octahedral complex ion.

Introduction

The question of the existence of a *trans* labilizing effect of certain ligands in octahedral complexes has recently come under serious study (Halpern, Palmer & Blakely, 1966). The nitrite ion (coordinated in the nitro form) is one of the more strongly *trans* labilizing ligands in square planar d^8 complexes (Cotton & Wilkinson, 1966). Llewellyn, O'Connor & Odell (1964) have observed, however, that the nitrite ion does not appear to have any kinetically observable labilizing effect on an NH_3 group *trans* to it in the nitropentamminocobalt(III) ion. Since the kinetic data of Halpern *et al.* seem to point to an S_N1-type mechanism for the replacement reaction involving the NH_3 group *trans* to a ligand $[Co(NH_3)_5X]^{n+}$, a *trans* effect which is attributable to anything other than stabilization of the five-coordinate intermediate by X should be observed as a lengthening of the Co–N bond *trans* to X. We have, therefore, undertaken a study of acidopentammines of cobalt in an attempt to demonstrate the existence or non-existence of what might be termed a 'structural' octahedral *trans* effect. Our general objective is to determine whether there is any correlation between kinetically observed or unobserved *trans* effects and the presence or absence of bond lengthening in the ground state of the reactant complex.

Experimental

Preparation of compound

Crystals of $[Co(NH_3)_5NO_2]Br_2$ were obtained by allowing a saturated solution of potassium bromide to diffuse through an ultrafine fritted disk into a saturated aqueous solution of $[Co(NH_3)_5NO_2](NO_3)_2$. Under these conditions crystallization was slow enough that a moderate diffusion rate could be used and crystals suitable for X-ray studies could be obtained within 4–6 hours.

X-ray crystallographic study

The orange-yellow rhombs were examined on a precession camera and were found to belong to the monoclinic system with the following cell dimensions: (Mo $K\alpha$, $\lambda=0{\cdot}7107$) $a=10{\cdot}71\pm0{\cdot}02$, $b=8{\cdot}791\pm0{\cdot}015$, and $c=11{\cdot}01\pm0{\cdot}02$ with $\beta=94°40'$. The density was measured by flotation in a methylene iodide–carbon tetrachloride mixture as $2{\cdot}258$ g.cm^{-3} which, for a unit-cell volume of 1033 Å^3 and a formula weight of 349·9 amu, gives 4·01 formula weights per cell.

The only systematic absences observed on the precession photographs were $k\neq2n$ and $k\neq2n+1$ for $0kl$ and $1kl$ respectively, giving the general condition for reflection $h+k=2n$, and $l\neq2n$ for $h0l$, determining the space group as either Cc or $C2/c$.

The intensities of 1324 reflections, $0<2\theta<56°$, were collected on a General Electric XRD-5 manual diffractometer, equipped with a eucentric goniometer head and scintillation counter, using Mo $K\alpha$ radiation. The moving-crystal, moving-counter method (θ-2θ scan) was used with a 2θ scan range of 2·66°. A crystal approximately 0·2 mm on an edge (equidimensional) was mounted on a glass rod with the b^* axis parallel to the φ axis. Data reduction was begun by selecting the statistically acceptable reflections on the criterion that observed intensity (peak-background) must be $\geq3\sigma$ where $\sigma=\sqrt{\text{peak}+\text{background}}$. The 667 reflections so selected were then corrected for absorption, $\mu=95$ cm^{-1}, using the spherically averaged approximation method of Bond (1959) taking μR as 0·7. Lorentz and polarization corrections were then applied.

Solution and refinement of the structure

A three-dimensional Patterson synthesis was calculated, using the program of Shoemaker, Katz & Seff (1962). Large peaks appeared on the two Harker lines of the type $0,2y,\frac{1}{2}$ which arise from $C2/c$. It was possible to assign these as Co–Co and Br–Br vectors, assuming the cobalt atoms to lie on the twofold axis and the bromine atoms to be in general positions. Another Br–Br peak appeared on the section $2x,0,\frac{1}{2}+2z$ to give a self-consistent solution with the initial positional parameters: Co, $x=0$, $y=0{\cdot}285$, $z=0{\cdot}2500$; Br, $x=0{\cdot}208$, $y=0{\cdot}002$, $z=0{\cdot}010$.

One cycle of least-squares refinement (where the function minimized was $\Sigma\omega||F_o|-|F_c||^2$) was carried out with use of the atomic form factors from the *International Tables for X-ray Crystallography* (1962) and allowing the cobalt and bromine positional and isotropic thermal parameters to be varied. The standard R_1 factor $(=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$ was then at 0·452. A difference Fourier synthesis was then calculated (Shoemaker, Katz & Seff, 1962) to locate the nitrogen and oxygen atoms. Two more cycles of refinement of all positional and isotropic thermal parameters using the program of Prewitt (1962) gave $R_1=0{\cdot}124$. At this point an anomalous dispersion correction for cobalt and bromine was applied (*International Tables*, 1962) and full anisotropic refinement was begun. Five cycles of full-matrix least-squares refinement with all reflections given equal (unit) weight brought the residual, R_1, to 0·08.

A weighting scheme was then introduced so that each F_o was weighted by an amount $\omega=\sigma^{-\frac{1}{2}}$ where $\sigma=(66{\cdot}03-3{\cdot}62|F_o|)^{\frac{1}{2}}$ for $|F_o|\le 17$, $\sigma=2{\cdot}72$ for $17<|F_o|<41$ and $\sigma=(0{\cdot}59|F_o|-15{\cdot}76)^{\frac{1}{2}}$ for $41\le|F_o|$. This scheme essentially removed the dependence of $\omega\Delta^2$ on F which had been previously observed. Final convergence of $\sqrt{\Sigma\omega\Delta^2/(\text{observations}-\text{parameters})}$ to a value of 1·058 was obtained. The weighted residual, $R_2=\Sigma\omega||F_o|-|F_c||/\Sigma\omega|F_o|$, had a final value of 0·10. The final calculated structure amplitudes, observed structure amplitudes, $|F_o|$'s and the $|F_c|$'s are listed in Table 1.

A final difference Fourier synthesis showed no peaks higher than about 0·6 e.Å^{-3} with a standard deviation, calculated according to the method of Cruickshank (1949), of 0·12 e.Å^{-3}.

The final fractional coordinates of all atoms in the asymmetric unit are listed in Table 2 with their estimated standard deviations (e.s.d.'s). The e.s.d.'s (σ's) were obtained from the usual least-squares formula, $\sigma_j^2=a_{jj}\,(\Sigma\omega\Delta^2)/(m-n)$, in which a_{jj} is the diagonal element corresponding to the parameter j in the matrix inverse to the normal equation matrix. Anisotropic thermal parameters, the β_{ij} in the expression $\exp\,[-(\beta_{11}h^1+\beta_{22}k^1+\beta_{33}l^1+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$, are listed in Table 3.

Table 2. *Fractional atomic coordinates and their e.s.d.'s**

	x/a	y/b	z/c
Br	0·2083(2)	0·0144(2)	0·0096(2)
Co	0·0	0·2876(3)	0·2500
N(1)	0·0	0·0631(19)	0·2500
N(2)	0·1834(13)	0·2875(16)	0·2470(12)
N(3)	0·0119(13)	0·2926(15)	0·4278(12)
N(4)	0·0	0·5065(21)	0·2500
O(1)	0·0707(18)	0·5769(16)	0·1878(16)

* E.s.d.'s, occurring in the last significant figure, are given in parentheses.

Table 1. *Observed and calculated structure amplitudes multiplied by* 48·6

H	K	FOBS	FCAL
****L = 0*******			
2	0	493	551
4	0	6272	5696
6	0	2478	2516
10	0	3114	2944
14	0	1073	1224
1	1	934	512
3	1	4759	4455
5	1	3788	3480
7	1	3211	3100
9	1	1317	1425
11	1	744	666
0	2	3097	3368
2	2	5808	5404
4	2	515	558
6	2	1862	1761
8	2	2133	2027
10	2	887	804
12	2	1585	1723
1	3	3486	3016
3	3	2082	1930
5	3	5103	4804
7	3	1844	1744
9	3	2040	1956
0	4	6074	5838
2	4	2261	2120
4	4	3789	2972
6	4	1280	1320
10	4	1834	1924
1	5	1202	1198
3	5	3759	3750
7	5	3376	3315
11	5	1149	1052
0	6	1937	1995
2	6	2485	2606
4	6	1073	1036
8	6	719	739
10	6	854	936
1	7	1990	2031
5	7	2507	2549
7	7	674	802
9	7	1072	1132
0	8	841	934
2	8	1762	1873
3	9	1488	1666
7	9	1437	1437
0	10	1328	1580
4	10	756	865
6	10	674	570
****L = 1*******			
-1	1	2609	2511
1	1	3461	3245
3	1	717	945
-3	1	2110	2289
5	1	2719	2504
-5	1	3029	2889
7	1	1291	1336
-7	1	1449	1636
9	1	788	736
-9	1	1151	1237
-11	1	801	894
11	1	923	946
0	2	487	350
-2	2	586	769
2	2	913	718
4	2	1211	1077
-6	2	1728	1738
8	2	759	826
-10	2	794	637
1	3	1171	1324
-1	3	3796	3590
3	3	1949	2041
5	3	861	827
-5	3	1265	1400
-7	3	844	789
9	3	746	635
-11	3	1241	1038
0	4	3652	3407
-2	4	1248	1202
2	4	2836	2786
4	4	723	686
-4	4	2508	2593
6	4	2312	2245
-8	4	1445	1480
-10	4	681	569
10	4	1024	1055
-12	4	959	679
-1	5	897	805
1	5	2027	2058
3	5	632	758
-3	5	1687	1704
-5	5	685	620
5	5	1260	1194
-9	5	720	847
11	5	750	738
0	6	1280	1457
-2	6	1791	1841
-6	6	2278	2324
8	6	1333	1330
-10	6	786	1394
-1	7	1263	1208
1	7	1656	1765
3	7	932	905
-3	7	1028	1143
0	8	1051	1088
2	8	1126	1244
-4	8	1855	2047
6	8	1757	1857
-8	8	1242	1351
10	8	803	883
1	9	676	839
-1	9	1625	1664
3	9	1120	1268
-5	9	759	925
7	9	677	318
-7	9	758	654
-2	10	964	1092
4	10	1071	1242
-6	10	1120	1241
1	11	1210	1362
-3	11	841	908
****L = 2*******			
0	0	995	1098
-2	0	6205	6241
2	0	7026	7775
-6	0	1420	1408
6	0	2180	2189
8	0	1581	1642
-8	0	2782	2528
12	0	1867	1834
-12	0	2076	2063
1	1	1808	2257
-1	1	2351	2926
3	1	2239	2178
-3	1	3478	4003
-5	1	3853	3778
5	1	4038	4046
-7	1	2692	2701
7	1	2914	2840
-9	1	1623	1548
9	1	1806	1751
11	1	694	435
0	2	6337	6143
-2	2	3676	3701
2	2	5098	4916
-4	2	2714	2698
4	2	2717	2714
6	2	632	560
-6	2	1749	1680
8	2	668	739
-8	2	1103	1039
10	2	1829	1705
-10	2	2313	2218
12	2	740	897
-12	2	1002	785
-1	3	815	822
3	3	2628	2604
-3	3	3410	3542
-5	3	2229	2243
5	3	2296	2287
-7	3	2970	2845
7	3	3094	2935
-9	3	888	796
9	3	1228	1249
11	3	975	843
-13	3	612	555
0	4	2479	2513
2	4	3843	3882
-2	4	4084	3791
4	4	1114	1137
-6	4	746	797
6	4	1172	1135
8	4	1313	1224
-8	4	1823	1772
-10	4	811	774
-12	4	1268	1363
12	4	1302	1294
1	5	1657	1657
-1	5	2930	2622
3	5	1000	1224
-3	5	1072	1070
5	5	3474	3519
-5	5	4236	4175
7	5	1037	1157
-9	5	1600	1617
9	5	1708	1724
-11	5	664	593
0	6	3059	3085
2	6	1697	1791
-2	6	1974	1863
-4	6	716	708
4	6	1405	1571
-8	6	837	873
10	6	947	914
-10	6	1075	1101
3	7	1571	1708
-3	7	1714	1752
5	7	843	940
-5	7	1142	1136
7	7	1548	1591
-7	7	1562	1568
9	7	749	602
0	8	1913	1978
-2	8	975	1035
2	8	1013	1028
4	8	917	1049
-10	8	796	824
1	9	812	963
-1	9	1435	1300
5	9	1306	1599
-5	9	1621	1786
-2	10	1031	975
2	10	1138	1083
****L = 3*******			
1	1	656	967
-1	1	1838	2057
3	1	558	690
5	1	1281	1326
-5	1	1829	1913
7	1	1065	926
9	1	889	737
-11	1	755	803
11	1	757	647
2	2	487	458
4	2	678	671
-4	2	1124	1385
6	2	982	921
-8	2	668	474
-10	2	399	109
10	2	729	544
-1	3	449	397
1	3	2416	2534
5	3	1432	1540
-9	3	690	731
11	3	701	743
0	4	1550	1596
2	4	878	972
-2	4	1409	1330
4	4	1987	2079
-6	4	1749	1724
8	4	935	1128
-10	4	929	920
1	5	948	967
-1	5	2300	2052
3	5	1168	1298
-3	5	758	969
-7	5	780	693
-11	5	751	722
0	6	1214	1265
-2	6	556	485
2	6	871	922
-4	6	1837	1820
6	6	1782	1730
-8	6	958	980
10	6	897	941
1	7	1153	1266
-1	7	1450	1327
-3	7	938	815
3	7	1104	1181
-2	8	1510	1372
4	8	1165	1359
-6	8	1749	1670
8	8	1218	1138
-10	8	722	670
-1	9	693	721
1	9	1281	1433
3	9	816	800
-3	9	978	1058
5	9	731	749
0	10	804	717
-2	10	746	352
2	10	823	783
-4	10	957	1083
6	10	941	1138
-1	11	907	988
3	11	481	890
****L = 4*******			
0	0	7999	7948
2	0	1345	1697
-2	0	2016	2174
-4	0	2349	2394
4	0	4881	5072
6	0	1420	1428
-6	0	1936	2296
-8	0	837	756
10	0	2201	2204
-10	0	2786	2585
1	1	789	719
3	1	2762	2861
-3	1	3106	3056
5	1	2127	2187
-5	1	2815	3275
-7	1	2022	2475
7	1	2865	2911
-9	1	920	766
9	1	1589	1512
11	1	929	840
0	2	2655	2584
-2	2	3187	3574
2	2	3887	4153
4	2	1766	1757
6	2	1669	1707
8	2	1163	1100
-8	2	1690	1628
-10	2	1190	1123
-12	2	1405	1268
12	2	1470	1516
1	3	1041	1106
-1	3	2977	2710
3	3	1316	1369
-3	3	2377	2523
-5	3	3187	3677
5	3	3318	3406
-7	3	1289	1676
7	3	1706	1742
-9	3	973	1129
9	3	1809	1853
0	4	4723	4545
-2	4	1450	1331
2	4	2190	2297
-4	4	1554	1766
4	4	2637	2699
-6	4	1363	1465
-8	4	977	879
10	4	1570	1497
-10	4	1672	1649
-12	4	889	576
1	5	1237	1378
3	5	2183	2141
-3	5	3793	3431
5	5	624	718
-7	5	2128	2255
7	5	2541	2645
11	5	888	1121
0	6	2159	2014
-2	6	1539	1417
2	6	2288	2410
-4	6	771	712
4	6	1000	974
-6	6	690	411
-8	6	929	990
1	7	943	894
-1	7	1661	1426
-3	7	1536	1425
-5	7	1971	1921
5	7	2054	2172
-7	7	621	739
7	7	689	690
9	7	1065	1121
0	8	1161	1104
-2	8	1065	1018
2	8	1556	1610
6	8	632	454
1	9	757	792
3	9	1031	1152
-3	9	1542	1501
-7	9	948	1040
7	9	1331	1247
0	10	1217	1215
4	10	823	799
****L = 5*******			
-1	1	2470	2360
1	1	2642	2889
3	1	795	1035
-3	1	1851	1902
5	1	1797	2022
-5	1	2018	2085
-7	1	669	965
7	1	1194	1147
9	1	855	791
-11	1	756	628
11	1	1082	944
0	2	966	1049
-2	2	1426	1440
4	2	632	717
-6	2	964	1077
8	2	845	673
-1	3	1631	1731
3	3	1732	1866
-5	3	619	1002
5	3	971	1005
-7	3	625	915
7	3	918	876
9	3	686	661
-11	3	835	827
-13	3	356	115
2	4	1606	1735
4	4	973	927
-4	4	1897	2016
6	4	1966	2119
-8	4	1057	1230
10	4	981	1064
1	5	1812	1930
3	5	620	643
-3	5	1469	1255
5	5	1093	1055
0	6	945	1106
2	6	631	727
-2	6	2047	1762
4	6	1713	1606
-6	6	1613	1735
8	6	1211	1267
-10	6	830	725
-1	7	1053	951
1	7	1381	1404
-3	7	843	648
3	7	885	840
5	7	753	713
-9	7	677	593
0	8	1288	1396
2	8	684	944
-4	8	2061	1807
6	8	1562	1527
-8	8	889	901
-1	9	1382	1466
3	9	1262	1185
-2	10	1167	910
4	10	983	978
****L = 6*******			
-2	0	3923	3724
2	0	4835	5358
-4	0	1471	1495
-6	0	860	1262
6	0	2612	2754
8	0	1374	1208
-8	0	2595	2687
12	0	1148	1489
-12	0	1794	1615
-1	1	2184	2111
-3	1	2119	2822
-5	1	2682	3154
5	1	2827	2811
-7	1	1074	1299
7	1	1725	1778
-9	1	1052	1024
9	1	1685	1660
0	2	5137	5045
2	2	1999	2155
-4	2	1259	1698
4	2	2777	2999
-6	2	1498	1864
-8	2	890	993
10	2	1450	1397
-10	2	1490	1870
-1	3	632	606
1	3	1564	1479
3	3	1741	1789
-3	3	2890	3223
5	3	946	1049
-5	3	1359	1338
-7	3	1793	2045
7	3	2402	2414
11	3	888	987
0	4	1234	1082
-2	4	2599	2669
2	4	3510	3305
-4	4	800	684
4	4	979	989
6	4	1292	1371
-8	4	1439	1606
-12	4	1042	1036
1	5	1474	1495
-1	5	3462	3119
5	5	2612	2643
-5	5	3361	3789
-9	5	873	1126
9	5	1743	1578
0	6	1678	1706
-2	6	1416	1311
2	6	1650	1743
4	6	1403	1419
-6	6	883	662
-8	6	756	734
1	7	1013	934
3	7	1146	1202
-3	7	1892	1706
-7	7	1337	1345
7	7	1469	1522
0	8	1421	1354
-2	8	694	540
2	8	758	826
4	8	943	1057
-6	8	745	657
1	9	802	758
-1	9	1485	1381
5	9	1217	1267
-5	9	1428	1424
-2	10	755	755
2	10	969	1059
****L = 7*******			
1	1	1117	1407
3	1	864	995
5	1	947	990
-5	1	1431	1504
7	1	687	706
-11	1	932	829
0	2	1145	1148
-4	2	763	978
-10	2	616	215
1	3	1191	1389
-3	3	661	655
-5	3	950	1012
5	3	1196	1229
-9	3	879	825
0	4	801	745
2	4	757	692
-2	4	1239	1288
4	4	1230	1225
-6	4	1738	1697
8	4	756	917
1	5	591	365
-1	5	1445	1431
3	5	1052	1118
-3	5	812	581
0	6	1545	1399
-4	6	1922	1551
6	6	1154	1280
-8	6	729	810
-1	7	838	762
1	7	952	836
3	7	1031	936
-2	8	1414	1333
4	8	823	915
-6	8	1353	1253
1	9	1268	1264
-3	9	893	707
****L = 8*******			
0	0	3615	3603
2	0	1690	1840
-4	0	1239	1328
4	0	2505	2754
-8	0	644	534
8	0	758	429
10	0	1215	1140
-10	0	1748	1831
1	1	786	620
3	1	619	808
-3	1	2572	2374
5	1	1045	1224
-5	1	1795	1548
-7	1	1319	1511
7	1	1822	1817
9	1	1030	1079
11	1	880	730
0	2	1529	1252
-2	2	1798	1559
2	2	2604	2694
4	2	1474	1458
6	2	1231	1325
-8	2	1237	1253
-12	2	944	860
-3	3	1757	1821
5	3	1705	1747
-5	3	1825	2176
-7	3	814	874
7	3	1119	1193
9	3	1313	1187
0	4	2656	2615
2	4	1377	1469
4	4	1751	1885
-6	4	1068	1226
-8	4	873	691
-10	4	1168	1185
10	4	1177	774
1	5	1381	1344
3	5	937	994
-3	5	1967	2131
-5	5	772	535
-7	5	1195	1246
7	5	1427	1546
0	6	1284	1320
-2	6	648	681
2	6	1273	1308
4	6	875	948
-8	6	897	804
-1	7	1242	1072
-3	7	873	890
5	7	1311	1156
-5	7	1694	1423
0	8	800	733
2	8	824	928
3	9	705	593
-3	9	1177	979
****L = 9*******			
1	1	1143	1211
5	1	799	972
0	4	1092	978
-4	4	1058	1219
6	4	980	1021
1	5	1237	1073
5	5	762	768
-2	6	982	847
4	6	716	712
-6	6	1145	877
-1	7	833	594
1	7	904	752
0	8	956	949
-4	8	1008	953
****L = 10*******			
0	0	743	286
-2	0	2011	1600
2	0	2655	2537
4	0	776	619
-4	0	1439	1215
6	0	1770	1775
-8	0	1357	1416
-1	1	1870	1572
-3	1	1827	1339
5	1	1120	1157
-5	1	1983	1754
7	1	1041	919
9	1	1105	1029
0	2	2472	2266
2	2	1191	1183
4	2	1879	1879
-6	2	978	1105
-8	2	718	801
-10	2	1016	1006
1	3	1233	1043
3	3	676	570
-3	3	1103	1634
-5	3	814	781
7	3	1516	1329
2	4	1973	1845
6	4	957	1073
-8	4	1122	941
1	5	697	561
-1	5	1523	1728
5	5	1354	1416
-5	5	1575	1603
0	6	1040	868
2	6	1034	1063
4	6	829	847
-6	6	752	581
-3	7	1265	1046
2	8	801	536
****L = 11*******			
1	1	1030	939
3	1	760	750
7	1	750	623
1	3	982	934
-5	3	818	787
5	3	824	813
0	4	755	592
2	4	767	613
-2	4	872	981
-6	4	895	940
3	5	758	668
0	6	1016	1009
-4	6	1007	965
****L = 12*******			
0	0	2185	2032
4	0	1707	1603
-6	0	1922	1470
1	1	815	765
-3	1	1674	1379
-7	1	825	605
2	2	1615	1453
6	2	917	1042
-8	2	923	843
-1	3	1420	1203
5	3	895	849
-5	3	1016	1190
0	4	1297	1278
4	4	1216	1139
-6	4	959	892
1	5	1162	1095
-3	5	1113	1223
****L = 13*******			
1	1	756	635
0	4	956	711
****L = 14*******			
2	0	1177	1012
-1	1	1076	814
0	2	1857	766

Table 3. *Anisotropic thermal parameters and their e.s.d.'s** × 10^4

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	59(2)	76(2)	58(2)	8(2)	− 2(1)	−1(1)
Co	41(3)	53(4)	39(2)	0	−2(2)	0
N(1)	77(20)	34(18)	57(24)	0	33(17)	0
N(2)	47(12)	109(20)	36(10)	9(13)	−2(8)	−17(11)
N(3)	60(12)	83(17)	34(12)	−15(13)	10(9)	−9(11)
N(4)	51(16)	84(22)	25(14)	0	9(11)	0
O(1)	144(22)	99(18)	99(18)	2(18)	44(16)	28(15)

* E.s.d.'s in parentheses.

Results

A projection of the complex ion, $[Co(NH_3)_5NO_2]_2^+$, onto a plane defined by N(2), N(3) and N(4) is shown in Fig. 1, which also indicates the numbering scheme. The bond lengths and bond angles with their e.s.d.'s are listed in Table 4. A projection of the contents of one unit cell onto the (010) plane is presented in Fig. 2, and pertinent intermolecular contacts (*i.e.*, those ≤4·5 Å) are listed in Table 5. The contents of Tables 4 and 5 were obtained using programs written by Wood (1964) and Shoemaker (1963).

Table 4. *Bond distances, angles and non-bonded intramolecular contacts*

N(1)-Co	1·976 Å	0·019 Å
N(2)-Co	1·985	0·015
N(3)-Co	1·972	0·016
N(4)-Co	1·921	0·021
N(4)-O(1)	1·161	0·022
N(1)-Co-N(2)	89·75°	0·45°
N(1)-Co-N(3)	91·21	0·52
N(2)-Co-N(3)	82·54	0·62
N(2)-Co-N(2′)	97·46	0·63
Co-N(4)-O(1)	123·01	0·98
O(1)-N(4)-O(1′)	113·9	1·9

Intramolecular contacts

N(2)	N(3)	2·610 Å
	N(3′)	2·974)
	N(1)	2·794
	N(4)	2·768
	O(1)	2·952
N(3)	N(1)	2·820
	N(4)	2·724
N(3′)	O(1)	2·969
O(1)	O(1′)	2·114

Table 5. *Intermolecular contacts not exceeding* 4·5 Å

Co	Br(x, y, z)	4·328 Å
	Br$(x-\frac{1}{2}, \frac{1}{2}+y, z)$	4·403
	Br$(x, -y, \frac{1}{2}+z)$	4·375
N(1)	Br(x, y, z)	3·625
	Br$(x, -y, \frac{1}{2}-z)$	3·544
	N(2) $(x-\frac{1}{2}, y-\frac{1}{2}, z)$	4·152
N(2)	Br(x, y, z)	3·568
	Br$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·465
	Br$(x, -y, \frac{1}{2}+z)$	3·912
	Br$(\frac{1}{2}-x, \frac{1}{2}-y, -(1+z))$	3·583
N(3)	Br$(-x, y, \frac{1}{2}-z)$	3·503
	Br$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·598
	Br$(x, -y, \frac{1}{2}+z)$	3·496
	Br$(x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$	3·836
	N(3) $(-x, -y, -z)$	4·001
N(4)	Br$(x-\frac{1}{2}, \frac{1}{2}+y, z)$	3·927
	Br$(x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$	4·403
	N(2) $(x-\frac{1}{2}, \frac{1}{2}+y, z)$	4·175
	N(3) $(x, -y, z-\frac{1}{2})$	3·981
O(1)	Br$(x-\frac{1}{2}, \frac{1}{2}+y, z)$	4·214
	Br$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·993
	Br$(\frac{1}{2}-x, \frac{1}{2}-y, -z)$	3·440
	N(2) $(-x, y, \frac{1}{2}-z)$	3·850
	N(2) $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·246
	N(3) $(x, -y, z-\frac{1}{2})$	3·083
	N(1) $(x, 1+y, z)$	4·390
Br	O(1) $(-x, -y, -z)$	4·458
	Br$(-x, -y, -z)$	4·458
	Br$(\frac{1}{2}-x, \frac{1}{2}-y, -z)$	4·247

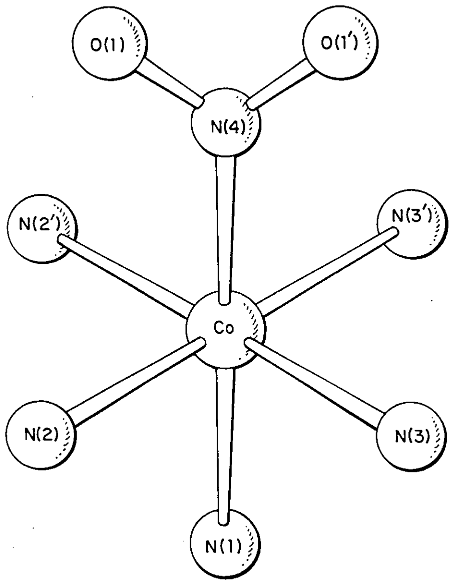

Fig. 1. Projection of the $[Co(NH_3)_5NO_2]^{2+}$ structure on the plane passing through N(2), N(3) and N(4).

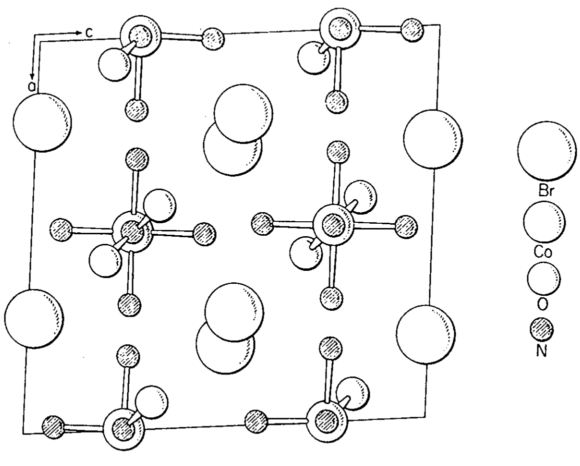

Fig. 2. Projection of the unit-cell contents on the 010 plane.

The atoms N(1), Co and N(4) lie on the crystallographic twofold axis and the complex ion has rigorous crystallographic symmetry 2. Its virtual symmetry (neglecting hydrogen atoms) approximates closely to *mm*, with one of the mirrors containing the NO_2 group and bisecting the N(2)–Co–N(3) angle. The substantial difference between the two sets of N–Co–N angles amongst the ligands *cis* to the nitro ligand (82·5° and 97·5°) is, perhaps, surprising. The oxygen atoms of the nitro group lie over the two larger angles and there may be some O···N interaction tending to enlarge these angles. The rather large thermal parameters for the oxygen atoms may contribute to this effect.

There appears to be little evidence of significant hydrogen bonding in this structure, though it is difficult to rule out the existence of some weak hydrogen bonds. A weak one may exist between O and N(3), which lie 3·08 Å. apart. The various N to Br distances (Table 5) are equal to or greater than the approximate sum of van der Waals radii (~3·5 Å) and at least 0·2 Å greater than what might be expected for a fairly normal N–H···Br bond. A check on the angles (Br–N–Br or Br–N–Co) at N(1), N(2) and N(3) showed that few were very close to optimum, though in one case, namely Co–N(3)–Br–$(x,\bar{y},\frac{1}{2}+z)$, the angle (109°) is quite satisfactory and the N–Br distance (3·50) is one of the shorter ones.

The most important feature of this structure is the lack of any significant difference between the Co–N(1) bond length and the other four Co–N bond lengths. The mean of value the latter four is 1·978 ± 0·010 Å while Co–N(1) is 1·976 ± 0·019 Å. Evidently the nitro ligand does not significantly weaken the bond *trans* to itself, Co–N(1), relative to the other four which are *cis* to it. In fact, the presence of the nitro ligand does not appear to have any significant influence on the Co–NH_3 bonds at all since the average value of the five bond lengths in this complex, 1·978 ± 0·010 does not differ significantly from the mean of those in $[Co(NH_3)\ ]^{3+}$, 1·96 ± 0·02, as reported by Barnet, Craven, Freeman, King & Ibers (1966) or the mean of those in $[Co(NH_3)_5Cl]^{2+}$, 1·99 ± 0·01, as reported by Stanko & Paul (1967).

The absence of any *trans* bond-weakening effect in $[Co(NH_3)_5NO_2]^{2+}$ is in full agreement with the kinetic data of both Halpern, Palmer & Blakely (1966) and Llewellyn, O'Connor & Odell (1964). In the case of $[Co(NH_3)_5SO_3]^{+}$, an appreciable kinetic *trans* effect has been observed (Halpern *et al.*, 1966) and a crystallographic study of a salt of this complex cation has been initiated to see if a 'structural' *trans* effect is present as well.

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