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Chemistry of UO_2^{2+} Group. I. Molecular Structure of Dioxo-Dinitratobis (Triphenylarsineoxide)Uranium(VI)

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Some uranyl complexes with triphenylphosphine and triphenylarsine oxides as ligands have been reinvestigated. The crystal structure of Dioxo-dinitratobis(triphenylarsineoxide)uranium(VI) has been determined by X-ray diffraction. The crystals are monoclinic with $a = 11.09 \pm 0.04$, $b = 19.28 \pm 0.06$, $c = 10.88 \pm 0.04$ Å, $\beta = 128° 10' \pm 10'$, $Z = 2$, *space group* $P2_1/c$. *Intensities of 921 independent reflections were obtained photographically with* CuK_α *radiation. The structure was solved by three-dimensional Fourier syntheses and refined by was full-matrix least squares. The final R index 8.6%. The uranium atom is octacoordinated with two bidentate nitrate ions and two oxygens from ligands coordinated in the plane perpendicular to the uranyl group.*

Introduction

The nature of the bonding in complexes containing the UO_2^{++} group is still an open problem. The coordination of oxygen-containing ligands permits hexacoordination and sometimes pentacoordination[1,2] in an equatorial plane. The bonds and the angles in this plane may be strongly influenced by the chemical nature of the ligands.

The series of compounds $UO_2(NO_3)_2X_2$, in which X represents an oxide of triphenylphosphine or triphenylarsine has been intensively studied.[3,4,5,6,7] It should be noted that the identical complexes were obtained when the starting materials were triphenylphosphine or triphenylarsine.[8,9]

The possibility of bidentate nitrate groups in these oxide complexes was suggested by Bullock.[6] The present communication describes the crystal structure of the complex Dioxo-dinitratobis(triphenylarsineoxide)-uranium(VI).

Experimental Section

Reactions of uranyl nitrate hexahydrate with triphenylphosphine. (a) In ethyl ether: a solution (20 ml) of uranyl nitrate hexahydrate (500 mg) and triphenylphosphine (655 mg) immediately deposited at room temperature 304 mg of $UO_2(NO_3)_2.2Ph_3PO$; yield 32%. (b) In dioxane: a solution (10 ml) of uranyl nitrate hexahydrate (500 mg) and triphenylphosphine (524 mg) was stirred under reflux for 20-30 minutes. 850 mg of complex were collected from the cold solution by adding 100 ml of ethyl ether; yield 90%. (c) In ethanol: a solution (50 ml) of uranyl nitrate hexahydrate (500 mg) and triphenylphosphine (655 mg) was boiled for 30 minutes and then the solvent was evaporated to dryness. Only 47 mg of complex were isolated with a yield of 5%. This yield was increased by a longer reaction time.

Reactions of uranyl nitrate hexahydrate with triphenylarsine. (d) In ethyl ether: uranyl nitrate hexahydrate (500 mg) and triphenylarsine (765 mg) were dissolved in 20 ml of ethyl ether. The resulting solution was stirred for 20 minutes at room temperature; the yellow crystals of $UO_2(NO_3)_2.2Ph_3AsO$ slowly appeared; yield 30%. (e) In dioxane: using the procedure under (b) uranyl nitrate hexahydrate (500 mg) and triphenylarsine (612 mg) reacted giving 970 mg of complex; yield 97%. (f) In ethanol: using the procedure under (c) triphenylarsine was found to be inert towards uranyl nitrate. In n-butanol the yield was less than 0.2% and in cyclohexanol was 10%.

Analyses and physical properties of the pure compounds $UO_2(NO_3)_2.2Ph_3PO$ and $UO_2(NO_3)_2.2Ph_3AsO$ were in very good agreement with literature values.

Anal. Calcd. % for $C_{36}H_{30}O_{10}N_2P_2U$ C, 45.5; H, 3.2; N, 2.9; U, 25.0. Found % C, 45.9; H, 3.3; N, 3.1; U, 24.8.

Calcd. % for $C_{36}H_{30}O_{10}N_2As_2U$ C, 41.6; H, 2.9; N, 2 7; U, 22.9. Found % C, 41.2; H, 2.8; N, 2.7; U, 23.3.

Crystal data. From oscillation, Weissenberg and precession photographs the crystal data for $UO_2(NO_3)_2 \cdot 2(C_6H_5)_3AsO$ are as follows: Monoclinic, $a = 11.09 \pm 0.04$ Å, $b = 19.28 \pm 0.06$ Å, $c = 10.88 \pm 0.04$ Å, $\beta = 128° 10' \pm 10'$, $U = 1829$ Å^3, $F(000) = 996$, $FW = 1038.5$, $D_m = 1.90$ g.cm^{-3}, $D_x = 1.87$ g.cm^{-3}, $Z = 2$, Space group $P2_1/c$. Absent spectra h0l $l = 2n+1$, 0k0 $k = 2n+1$; $\mu = 183$ cm^{-1} for CuK_α radiation.

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(8) Some attempt was made to prepare the complex with triphenylamine also, but no product was obtained. However in alcohols as solvents the unaltered starting materials were recovered while in dioxane or ethyl ether some decomposition occurred.

(9) It is not clear whether atmospheric oxygen or the peroxides as impurities or the uranyl nitrate are responsible for the ligand oxidation.

Table I. Calculated and observed structure factors

0,0,L		
2	2806	2910
6	1209	1027
8	1057	1014
1,0,L		
0	1092	1295
2	1621	1364
-2	2131	2016
4	2011	1862
-4	2610	2749
6	1567	1579
2,0,L		
0	1740	1521
2	1745	1880
-2	1291	1095
4	1499	1589
-4	2213	2262
-6	1486	1567
3,0,L		
0	2388	2224
2	1627	1815
-2	558	544
-4	1146	907
-6	1709	1480
-8	1523	1517
4,0,L		
0	1158	1089
2	425	367
-2	1769	1952
4	1149	835
-4	1223	1129
-6	779	732
-8	903	894
5,0,L		
0	843	723
2	1130	907
-2	1389	1320
4	1008	941
-4	2552	2573
-6	1667	1466
6,0,L		
0	1444	1529
2	944	1002
-2	804	757
-4	772	641
-6	1533	1397
-8	1632	1517
7,0,L		
0	1014	1138
-2	1658	1448
-4	1094	890
-8	1110	832
-10	1164	1122
8,0,L		
-2	1060	801
-4	2163	1818
-6	1257	1068
9,0,L		
0	1129	1004
-6	1435	1321
-8	1226	1200
10,0,L		
0	854	906
-2	1138	1111
-8	1105	972
-10	974	979
11,0,L		
-4	1115	1190
-10	1083	896
12,0,L		
-6	1127	1039
-8	663	710
13,0,L		
-8	863	879
0,1,L		
2	833	-740
3	1151	1075
5	860	676
6	424	412
7	1147	1052
9	815	807
1,1,L		
1	359	88
-2	528	-576
3	946	978
-3	2562	2662
4	586	574
-4	502	385
5	1386	1437
-5	1362	1290
7	655	822
-7	708	643
-9	700	701
2,1,L		
1	880	849
-1	1230	1635
2	776	696
-2	1463	-1676
3	1616	1579
-3	1424	1632
5	1111	1048
-5	2097	2206
-6	668	476
-7	1039	966
3,1,L		
0	797	553
1	2009	2159
-1	1734	2171
2	672	-591
-2	1268	1203
3	694	652
-3	883	706
-4	283	-327
-5	1560	1507
-6	641	-729
-7	1100	1134
-9	618	705
4,1,L		
0	511	-470
1	994	919
-1	1423	1490
3	563	498
-3	990	1114
4	608	609
-4	862	786
5	832	830
-5	801	701
-7	461	513
-9	928	970
-11	621	568
5,1,L		
1	1019	1014
-1	908	907
-2	856	-731
3	903	851
-3	1351	1403
-4	448	-404
5	639	659
-5	1730	1767
-7	694	597
6,1,L		
1	1041	1186
-1	811	804
3	518	595
-3	567	484
-4	539	-507
-5	966	849
-6	585	-582
-7	1243	1223
-9	1016	992
7,1,L		
1	524	595
-1	1203	1281
-3	1244	-1176
-4	622	506
-5	1034	944
-7	925	742
-9	819	906
8,1,L		
-2	623	-452
3	642	598
-3	1288	1243
-5	1840	1708
-7	614	557
-9	586	521
-11	596	730
9,1,L		
1	732	814
-1	675	701
-3	551	446
-5	913	873
-7	1348	1167
-9	922	899
10,1,L		
-1	747	839
-3	953	886
-5	834	701
-7	651	708
-9	1032	1039
11,1,L		
-3	896	938
-5	656	733
-9	590	604
-11	645	730
12,1,L		
-7	992	804
13,1,L		
-7	538	609
-9	727	752
0,2,L		
0	1621•	1827
2	799	822
3	1220	1194
4	1239	1314
6	886	866
1,2,L		
1	640	-637
2	1031	1267
-2	806	837
3	1082	932
-3	856	833
4	864	948
-4	1404	1375
5	387	397
-5	707	808
6	1000	974
-6	925	940
-7	440	-458
-8	614	635
2,2,L		
0	1904	1906
1	1201	1258
-1	363	407
2	1267	1475
-2	1495	1617
-3	765	-628
4	1058	1012
-4	1333	1516
5	645	-535
6	1006	932
-6	568	598
-7	715	859
-8	661	503
3,2,L		
0	1210	932
1	336	263
-1	546	654
2	1231	1347
-2	774	956
3	716	-672
-3	354	345
4	906	979
-4	1165	1517
-5	736	-621
6	661	654
-6	859	949
-8	526	632
4,2,L		
0	1165	1014
1	701	-682
-1	610	-473
2	968	1007
-2	983	1144
3	507	499
-3	1295	1371
4	688	707
-4	905	1045
-5	674	718
-6	1083	1211
-7	379	-403
-8	806	965
5,2,L		
1	769	704
2	707	676
-2	1109	1154
-3	579	-609
-4	908	953
-6	935	1039
-7	802	752
-8	781	779
-10	614	567
6,2,L		
0	739	871
-1	478	485
2	756	674
-2	1008	1101
-4	1266	1332
-5	723	-672
-6	764	701
-8	604	652
-10	558	706
7,2,L		
0	718	383
2	583	704
-2	954	1013
-4	1283	1394
-6	1034	1131
-7	686	-707
-8	656	751
8,2,L		
0	697	969
-2	944	937
-4	975	992
-6	933	997
-7	454	425
-8	925	955
9,2,L		
-1	534	560
-2	876	853
-4	876	845
-5	809	-701
-6	809	964
-8	868	908
-10	737	822
10,2,L		
-2	504	574
-3	581	596
-4	933	909
-6	1138	1022
-8	745	720
-10	661	693
11,2,L		
-2	437	508
-4	481	574
-6	669	629
-8	650	681
-10	633	683
12,2,L		
-4	461	576
-6	539	578
-8	504	542
-10	430	605
13,2,L		
-4	386	524
-6	603	502
-8	452	541
-10	472	515
14,2,L		
-8	568	493
0,3,L		
1	1504	1641
2	775	-653
3	1932	1974
5	1222	1296
6	684	563
7	652	508
1,3,L		
0	543	-353
1	2166	2340
2	811	660
-2	467	297
3	2134	2185
-3	845	747
4	723	655
-4	962	950
5	608	547
-5	1422	1270
7	488	491
-7	1316	1317
9	869	750
2,3,L		
0	1356	1258
1	1530	1554
2	1034	922
3	617	504
-3	1550	1423
5	895	886
-5	739	639
-6	455	427
7	978	839
-7	833	955
-9	1004	982
3,3,L		
0	952	746
1	794	834
-1	1316	1406
-2	417	388
3	1349	1349
-3	1849	2219
5	1318	1289
-5	1770	1867
-6	412	-344
-7	609	373
4,3,L		
0	449	-473
1	2096	1961
-1	975	993
3	1128	1247
-3	706	794
-4	612	537
5	577	476
-5	1952	2062
-7	1411	1498
5,3,L		
1	1258	1326
-1	1819	1826
-3	1127	1217
-4	565	415
-5	288	343
-7	894	915
-9	1139	1256
6,3,L		
1	431	439
-1	1136	1157
3	760	715
-3	1692	1891
5	978	808
-5	1085	1143
-7	431	461
-9	636	566
-11	829	779
7,3,L		
1	1087	1010
-1	462	489
3	795	831
-3	853	834
-4	635	572
-5	1626	1709
-7	1246	1164
8,3,L		
1	891	964
-1	1149	1250
-3	606	642
-5	894	669
-7	1404	1299
-9	1210	1223
9,3,L		
-1	978	845
-3	1344	1347
-5	1019	963
-9	870	1006
-11	943	939
10,3,L		
-3	744	766
-5	1354	1147
-7	870	856
11,3,L		
-7	1225	1074
-9	842	838
-11	382	287
12,3,L		
-3	1087	798
-9	869	807
-11	869	724
13,3,L		
-5	978	776
0,4,L		
0	1510	213
1	906	845
2	1632	1512
3	480	312
4	2753	2482
6	1208	1031
1,4,L		
0	2875•	3080
1	552	492
2	2300	2306
-2	1046	937
4	942	878
-4	1088	1097
-6	1567	1472
-8	928	872
2,4,L		
0	1834	1601
-1	1165	-1225
2	1102	968
-2	2484	1645
-3	704	613
-4	1200	1184
-5	907	712
6	756	803
-6	739	642
8	725	666
-8	1388	1273
3,4,L		
0	561	376
1	562	432
2	878	725
-2	2658	2551
-3	727	690
4	1369	1374
-4	2525	2314
6	903	819
-6	824	767
4,4,L		
0	1542	1311
-1	517	414
2	1796	1808
-2	728	651
-4	1504	1353
-6	1932	1919
-8	904	1019
5,4,L		
0	1587	1691
2	749	589
-2	1894	1788
-3	665	549
-4	702	589
-5	470	-403
-6	969	941
-8	1452	1483
6,4,L		
0	674	586
-2	1635	1529
4	697	760
-4	2093	2013
-6	1120	840
-10	903	905
7,4,L		
2	791	906
-3	531	-463
-4	1487	1240
-6	1637	1471
-8	1143	970
8,4,L		
0	912	1062
-2	899	804
-6	930	754
-8	1552	1328
9,4,L		
-2	1315	1240
-4	1268	1164
-10	745	787
10,4,L		
-4	925	947
-6	1074	1063
11,4,L		
-6	933	848
-8	1119	1061
12,4,L		
-10	1047	889
0,5,L		
1	343	178
2	390	420
3	1806	2094
4	315	-251
5	1084	1105
6	686	-624
7	565	522
1,5,L		
0	1262	1247
1	1429	1576
-1	2004	2105
2	532	-404
-2	1168	1081
3	1201	1226
-3	858	893
4	919	-861
-4	343	-280
5	478	543
-5	910	927
-7	1139	1160
2,5,L		
0	660	-657
1	1371	1457
-1	1611	1900
2	514	-473
-2	414	369
3	876	840
-3	1233	1356
4	466	472
-4	728	551
5	547	570
-5	891	890
7	627	610
-7	703	822
-9	754	698
3,5,L		
0	490	404
1	711	714
-1	947	1086
2	990	999
-2	767	-773
3	967	1047
-3	1042	1211
-4	480	407
5	883	918
-5	1012	1050
-6	776	666
-7	587	685
-9	546	557
4,5,L		
0	1021	900
1	1403	1364
-1	1262	1319
3	838	883
-3	1495	1629
-4	835	-752
5	508	545
-5	1270	1377
-7	814	883
-8	565	630
-9	654	599
5,5,L		
0	335	-358
1	1047	1079
-1	1083	1109
2	430	-433
-2	291	292
3	641	676
-3	1043	1052
-4	336	433
-5	718	693
-6	701	-736
-7	1190	1200
-9	881	969
6,5,L		
0	640	-741
1	511	712
-1	964	1025
-2	639	-440
3	511	638
-3	1547	1530
-4	941	926
-5	1375	1333
-6	572	377
-7	895	924
-9	540	550
-10	544	-371
7,5,L		
1	646	612
-1	648	620
-2	438	-370
3	546	573
-3	1042	963
-4	844	-782
-5	1046	1045
-7	1050	1074
-8	663	554
-9	619	710
8,5,L		
1	670	691
-1	895	946
-2	754	712
-3	518	502
-5	577	442
-6	724	-768
-7	856	908
-9	670	770
9,5,L		
-1	427	516
-3	922	998
-5	874	903
-8	421	-352
-9	487	542
-11	524	618
10,5,L		
-3	631	648
-5	679	702
-7	645	704
11,5,L		
-7	776	865
-9	530	642
12,5,L		
-7	442	501
-9	534	592
0,6,L		
0	858	988
1	809	774
2	718	831
3	666	479
4	751	676
6	786	847
8	784	764
1,6,L		
0	1830	1584
1	469	413
-1	491	439
2	1118	1225
-2	1552	1696
3	638	-626
4	914	944
-4	1244	1289
5	463	-395
-5	559	-483
6	775	786
-6	584	505
-8	700	509
2,6,L		
0	978	990
1	957	-872
-1	790	-776
2	1609	1931
-2	916	975
-3	717	690
4	1109	1138
-4	1334	1420
5	582	508
-6	935	1054
3,6,L		
0	1577	1559
1	346	362
-1	701	-650
2	1513	1480
-2	1514	1773
3	516	598
4	668	669
-4	669	618
-5	631	547
-6	890	1003
-8	1005	1134
4,6,L		
0	1383	1300
1	595	513
-1	525	514
2	662	692
-2	2107	2279
-3	483	-413
4	599	775
-4	1236	1491
-5	641	-595
-6	857	816
-7	589	693
-8	454	639
5,6,L		
0	668	661
1	702	-644
2	1024	1225
-2	1150	1181
-3	1153	1137
4	1005	1003
-4	1413	1439
-6	1619	1242
-7	417	-452
6,6,L		
0	1168	1358
-1	515	-499
2	825	911
-2	987	983
-4	872	846
-5	449	506
-6	1430	1421
-8	1036	1114
7,6,L		
0	891	1020
-2	1224	1374
-3	837	-738
-4	1061	1114
-5	412	-433
-6	570	610
-8	1043	1042
8,6,L		
-2	1031	1054
-4	1063	1074
-6	947	845
-8	610	797
9,6,L		
-2	423	541
-4	991	900
-6	1199	1174
-8	739	830
10,6,L		
-8	894	981
11,6,L		
-4	661	799
-6	797	742
12,6,L		
-6	605	640
0,7,L		
1	1657	1499
3	1264	1062
5	355	398
7	1170	1014
1,7,L		
0	776	538
1	452	433
-1	1680	1731
3	1178	997
-3	2142	1719
5	1598	1303
-5	639	547
7	795	808
2,7,L		
1	1380	1351
-1	466	209
3	2083	2051
-3	1175	1046
5	876	863
-5	1715	1637
-7	936	878
3,7,L		
1	2066	1840
-1	2552	2335
3	645	628
-3	864	917
-5	965	780
-7	1500	1548
-9	954	945
4,7,L		
0	473	400
1	870	824
-1	1659	1731
3	670	558
-3	2342	2345
5	722	802
-5	1150	924
-9	1063	941
5,7,L		
1	695	668
-1	528	391
3	1436	1360
-3	1878	1851
5	926	753
-5	2039	1825
5,8,L		
1	379	443
5,7,L		
-7	1144	1127
6,7,L		
1	1282	1455
-1	1227	1184
3	622	674
-3	747	645
-5	1269	1080
-7	1826	1717
7,7,L		
1	744	667
-1	1696	1562
-3	1539	1306
-7	823	861
-9	1089	1043
8,7,L		
-1	523	554
-3	1658	1462
-5	1731	1517
-7	882	633
9,7,L		
1	733	715
-1	578	558
-5	1231	1043
-7	1444	1315
10,7,L		
-1	797	800
-3	693	641
-7	732	667
-9	1003	970
11,7,L		
-3	872	823
-5	805	776
12,7,L		
-5	793	666
-7	885	855
13,7,L		
-7	694	620
-9	797	763
0,8,L		
0	2003	1760
1	458	-394
2	1369	1319
4	608	585
5	503	410
6	755	723
8	770	816
1,8,L		
0	750	697
-1	492	-335
2	666	633
-2	1703	1628
-3	284	290
4	1059	914
-4	1316	1340
-5	489	391
6	862	827
-6	451	494
2,8,L		
0	874	780
1	530	499
2	1576	1560
-2	947	1126
-3	548	-370
4	1094	1039
-4	1385	1490
5	546	-341
-6	1162	1179
3,8,L		
0	1698	1779
-1	619	620
2	1321	1310
-2	1429	1500
-3	529	536
-4	499	453
-6	1040	1163
-8	1127	1291
4,8,L		
0	1105	1025
1	407	-262
-1	284	-220
2	477	398
-2	1904	2270
-3	639	535
4	909	708
-4	1277	1172
-6	414	390
5,8,L		
0	474	549
2	1004	1060
-2	860	794
-3	663	-616
4	1013	946
-4	1431	1450
-6	1373	1485
-7	508	516
6,8,L		
0	1104	1207
-1	776	667
2	834	899
-2	601	646
-4	740	668
-5	451	-362
-6	1479	1370
-8	1099	1136
7,8,L		
0	811	846
-2	1230	1234
-4	803	677
-5	357	419
-6	463	325
-8	901	900
-10	625	883
8,8,L		
-2	902	790
-4	1355	1198
-6	887	843
-8	587	497
9,8,L		
-4	502	537
-6	1126	1003
-8	837	743
10,8,L		
-2	667	778
-8	815	728
-10	665	668
11,8,L		
-4	644	764
-6	608	595
12,8,L		
-6	696	701
-8	520	549
0,9,L		
1	1215	1331
0,9,L		
2	794	-780
3	999	1115
5	833	894
1,9,L		
0	867	-838
1	1339	1525
-1	1164	1360
-2	529	-429
3	1129	1268
-3	1229	1317
4	693	617
-4	440	398
-5	953	1010
2,9,L		
0	733	614
1	1011	1060
-1	1189	1357
-2	421	-308
3	1022	990
-3	871	937
-4	815	-793
-5	737	876
3,9,L		
1	1122	1176
-1	890	1048
2	835	-803
-2	582	471
-3	930	1057
-5	839	1023
4,9,L		
0	719	-690
1	688	809
-1	899	1022
-3	1136	1364
-4	707	738
-5	1035	1006
-7	708	819
5,9,L		
1	829	981
-1	817	932
-2	680	-588
-3	1282	1463
-5	1219	1292
-7	1040	1031
6,9,L		
-1	1007	1140
-3	983	1178
-5	737	771
-7	985	1161
7,9,L		
-3	974	858
-5	819	922
8,9,L		
-3	705	743
-5	567	665
0,10,L		
0	1101	696
1	438	-410
2	1263	1135
4	1458	1439
1,10,L		
0	1166	1135
1	638	-521
-1	771	-752
2	1484	1616
-2	599	629
4	778	674
-4	1081	1046
-6	1092	1246
2,10,L		
0	1718	1510
1	544	445
2	834	735
-2	1930	1997
-3	522	-379
-4	716	762
3,10,L		
0	792	714
1	581	-546
2	655	710
-2	1552	1619
-4	1461	1447
-6	681	896
4,10,L		
0	1112	1162
2	1485	1433
-2	871	891
-3	396	395
-4	947	1030
-6	1287	1453
5,10,L		
0	1347	1533
-2	1247	1324
-4	707	599
-6	829	956
6,10,L		
-1	482	512
-2	1316	1343
-4	1382	1471
-6	581	735
7,10,L		
-2	617	542
-4	1077	1068
-6	1375	1446
8,10,L		
-2	891	875
-4	742	785
-6	892	840
9,10,L		
-4	819	800
0,11,L		
1	896	845
3	1383	1245
5	1218	1069
1,11,L		
1	1605	1674
-1	829	757
3	1325	1370
-5	795	883
2,11,L		
1	1172	1051
-1	2088	1960
-2	603	498
-3	951	849
3,11,L		
1	623	641
-1	811	684
3	1072	1062
-3	1696	1689
-5	1446	1303
4,11,L		
1	1339	1224
-1	655	572
-3	626	643
-5	1359	1229
-7	1210	1182
5,11,L		
1	1069	1051
-1	1538	1504
-3	814	774
6,11,L		
-1	965	845
3	979	677
-3	1628	1576
-5	907	861
7,11,L		
-5	1383	1229
-7	1010	1034
8,11,L		
-7	1020	1085
0,12,L		
0	1072	853
0,14,L		
0	1856	1869
0,16,L		
0	1282	1053
0,22,L		
0	566	707

The density was measured by the flotation method in a mixture of sym-tetrabromethane and sym-dichloroethane.

Intensity data. A regular prismatic *b* crystal about 0.05 mm. in diameter was selected for the X-ray work. Intensities were recorded for the layer k=0 to 11 using the multi-film and equi-inclination Weissenberg technique with nickel-filtered copper radiation (λ = 1.5418 Å). The hk0 and 0kl reflections were collected by the precession method. The intensities of the recorded 921 reflections were measured with a Joyce-Loebl Flying Spot microdensitometer. The intensities of the several layers were reduced to a common scale by comparison with common hk0 and 0kl (Precession) after applying the Lorentz and polarization factors. No correction was made for absorption (μR = 0.46) or extinction. The absolute scale and the approximate isotropic temperature factor were determined by a Wilson plot from the three-dimensional data and were edjusted when the structure became known.

Determination of structure. Considering that two molecules are to be placed in the unit cell, the two uranium atoms must lie on inversion centers and the 2a equipoint was chosen. The coordinates of the arsenic atom were readily obtained from P(uv) and P(uw). The three-dimensional electron density maps computed with the contributions of the heavy atoms yielded the positions of the remaining atoms.

The set of structure factors evaluated using the positional parameters of the trial structure and an overall temperature factor B of 2 Å^2 gave an R_{hkl} index of 16%.

Refinement. The Fourier coordinates were initially refined on an Olivetti Elea 6001 s by block-diagonal least-squares[10] with isotropic temperature factors using the Cruickshank weighting scheme. Atomic form factors for U, As, O, N, C, were taken from the International Tables for X-ray Crystallography (1962). The resulting R was 11.5%. The refinement was then continued on an IBM 7040-7094 system with the X-ray 63 program[11] using full-matrix least-squares[12] with isotropic temperature factors. The final refinement was made with two cycles, using anisotropic temperature factors for all atoms except N and those of the phenyl

Table II. Coordinates ($\times 10^4$) and their e.s.d.'s (in parentheses)

	x/a	y/b	z/c		x/a	y/b	z/c
U	0 (0)	0 (0)	0 (0)	C(6)	4917 (63)	1075 (36)	4483 (66)
As	3132 (4)	1385 (3)	1221 (5)	C(7)	4055 (44)	1185 (26)	316 (48)
O(5)	1017 (33)	—685 (20)	60 (34)	C(8)	5664 (60)	983 (31)	1371 (65)
O (4)	1422 (52)	—548 (27)	4477 (48)	C(9)	6300 (44)	706 (27)	682 (48)
O (3)	—80 (35)	—676 (22)	2019 (35)	C(10)	5549 (46)	710 (28)	—923 (49)
O (2)	1732 (42)	81 (27)	2983 (39)	C(11)	4068 (59)	887 (32)	—1883 (62)
O(1)	2181 (35)	723 (19)	1202 (37)	C(12)	3241 (51)	1334 (28)	—1253 (55)
N	1040 (39)	—400 (28)	3250 (56)	C(13)	1966 (47)	2209 (29)	282 (50)
C(1)	4656 (43)	1562 (26)	3365 (46)	C(14)	783 (38)	2350 (24)	330 (42)
C(2)	5630 (63)	2159 (36)	3822 (65)	C(15)	—100 (52)	3000 (25)	—200 (52)
C(3)	6764 (62)	2317 (36)	5451 (67)	C(16)	233 (90)	3550 (50)	—776 (94)
C(4)	6876 (75)	1886 (42)	6410 (80)	C(17)	1334 (79)	3383 (41)	—950 (79)
C(5)	6023 (66)	1316 (38)	6062 (69)	C(18)	2200 (48)	2792 (48)	—383 (86)

Table III. Thermal parameters ($\times 10^2$) and their e.s.d.'s (in parentheses)

(a) Anisotropic thermal factors ($\exp[-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*]$)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
U	200 (6)	164 (13)	287 (8)	— 47 (14)	164 (6)	— 13 (15)
As	182 (14)	312 (36)	211 (20)	— 13 (21)	122 (16)	20 (23)
O(1)	307 (138)	357 (293)	331 (148)	—108 (151)	206 (126)	— 66 (151)
O(2)	682 (193)	654 (345)	486 (180)	— 87 (250)	459 (165)	— 94 (243)
O(3)	398 (151)	758 (327)	295 (162)	—208 (180)	233 (140)	211 (183)
O(4)	954 (291)	1175 (370)	269 (189)	141 (262)	397 (203)	158 (213)
O(5)	286 (130)	431 (287)	301 (148)	—221 (154)	193 (122)	—145 (151)

(b) Isotropic thermal factors

	B (Å^2)		B (Å^2)		B (Å^2)
N	380 (80)				
C(1)	199 (84)	C(7)	204 (87)	C(13)	128 (95)
C(2)	454 (132)	C(8)	412 (124)	C(14)	94 (70)
C(3)	434 (134)	C(9)	240 (92)	C(15)	200 (78)
C(4)	493 (158)	C(10)	231 (89)	C(16)	900 (212)
C(5)	437 (137)	C(11)	453 (128)	C(17)	684 (172)
C(6)	503 (145)	C(12)	283 (109)	C(18)	800 (192)

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(10) G. Panattoni, G. Grubissich, and E. Frasson, *Ric. Sci.*, II-A, 35, 995 (1965).

(11) Stewart, Technical Report TR6Y-6, Univ. of Maryland, College Park, Maryland (1964).

(12) W. R. Busing, K. O. Martin, and H. A. Levy, ORHL-TM-305, Tennessy (1962).

groups. Various weighting functions were employed, at the different stages of the refinement. During the final cycles the weights w were set equal to 1 for $F_o < 100$ and equal to $\frac{10^4}{F_o^2}$ for $F_o \geqslant 100$ following a Hughes's modified scheme. The final R index was 8.6%. For the final cycle, the average ratio of the change in a parameter to its estimated standard deviation was 0.5 and the maximum ratio was 0.8. Observed and calculated structure factors are listed in Table I.

A final $F_o - F_c$ synthesis showed some ridges of electron density near the uranium atom extending in the *b* direction, along which the layers were recorded, but no appreciable residues were found over the rest of the unit cell.

Accordingly no allowance was made for the hydrogen atoms. The positional and thermal parameters with their estimated standard deviations are shown in Tables II and III.

Discussion

The isolated compounds (I) and (II) have the general formula $UO_2(NO_3)_2 \cdot 2L$ ($L = (C_6H_5)PO, (C_6H_5)_3AsO$).

The structure of (I) is the same as that of (II). This is shown by the similarity in composition, by the infrared spectra and by X-ray single crystal diffraction.[13]

The uranium atom is 8-coordinated. The uranyl group is surrounded equatorially by an irregular hexagon of six oxygen atoms with a configuration similar to that commonly observed in other uranyl complexes.[15] Figure 1 shows a perspective view of the molecule. Figure 2 shows the crystal packing in the cell. In Table IV are listed the intermolecular contacts less than 3.6 Å.

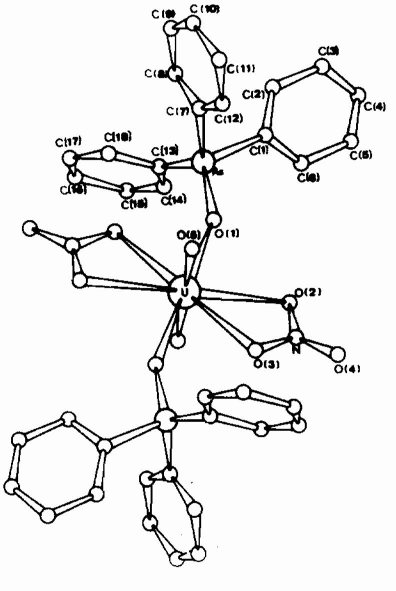

Figure 1. A perspective view of the molecule.

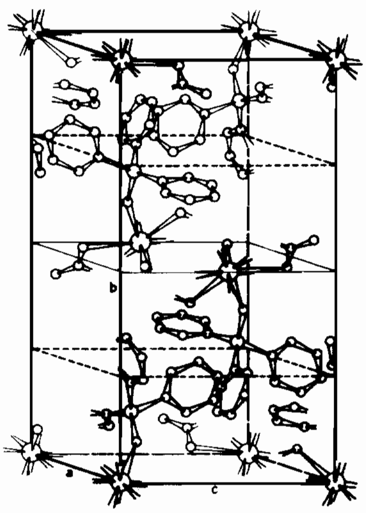

Figure 2. Molecular packing in the unit cell.

Table IV. Intermolecular contacts.

Atom 1	Atom 2	sym.	Dist.	Symmetry operation used in generating Atom 2
O(2)	C(17)	1	3.31 Å	
C(5)	O(2)	2	3.37	1 = x, ½—y, ½+z
C(5)	O(4)	2	3.55	
C(5)	O(5)	2	3.59	2 = 1—x, $\bar{y}$, 1—z
C(4)	N	2	3.55	
C(5)	N	2	3.36	3 = 1—x, $\bar{y}$, $\bar{z}$
C(9)	O(5)	3	3.53	
C(10)	O(5)	3	3.31	4 = $\bar{x}$, ½+y, ½—z
C(15)	O(4)	4	3.47	
C(16)	O(4)	4	3.40	
C(10)	C(8)	3	3.45	
C(9)	C(8)	3	3.56	
C(10)	C(9)	3	3.52	
C(11)	C(9)	3	3.46	
C(12)	C(9)	3	3.58	

Although the deviations of the oxygens from the L.S. equatorial mean plane are of the same order as the e.s.d.'s, their regularly alternating disposition suggests a slightly puckered structure.

The two nitrate ions, which are crystallographically equivalent, are coordinated as bidentate groups and are tilted with respect to the equatorial plane

Bond lengths and angles are reported in Tables V and VI.

The orientation of the phenyl rings in the triphenylarsine oxide moiety is described in Table VII.

The U–O bond length of the uranyl group, which is symmetrical and linear, is 1.71 Å, somewhat shorter than has been generally found in uranyl complexes but comparable with the reported distance 1.67 Å in uranyl carbonate.[14] The two $U–O_{(nitrate)}$ distances, 2.56 and 2.60 Å, are slightly longer than in uranyl nitrate hexahydrate[15] probably because of the different ligands.

The $U–O_{(ligand)}$ bond is 2.36 Å. This value is comparable with 2.39 and 2.38 Å for the $U–O_{(water)}$ distance in uranyl nitrate hexahydrate[15] and with a mean value of 2.36 Å of five U–O bonds in μ-*trans*-diacetato-bis (dioxo-triphenylphosphineoxide-acetato)-diuranium(VI), $(UO_2(OAc)_2 \cdot Ph_3PO)_2$[2]. This seems to

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(13) R. Graziani, B. Zarli and G. Bandoli, *Ric. Sci.*, *37*, 984 (1967).
(14) D. T. Cromer and P. E. Harper, *Acta Cryst.*, *8*, 847 (1955).
(15) (a) D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, *19*, 369 (1965); (b) J. C. Taylor and M. H. Mueller, *Acta Cryst.*, *19*, 536 (1965).

Table V. Intramolecular bond angles (°) and their e.s.d.'s (×10)

O(1)—U—O(2)	63.4 (16)	U—O(2)—N	98.7 (23)	O(1)—As—C(1)	103.5 (20)
O(2)—U—O(3)	49.5 (17)	U—O(3)—N	99.3 (26)	O(1)—As—C(7)	113.1 (22)
O(1)—U—O(5)	90.5 (15)	O(2)—N—O(3)	112.6 (29)	O(1)—As—C(13)	115.0 (23)
O(2)—U—O(5)	92.1 (16)	O(2)—N—O(4)	124.5 (31)	C(1)—As—C(7)	109.2 (23)
O(3)—U—O(5)	86.9 (15)	O(3)—N—O(4)	122.8 (30)	C(1)—As—C(13)	107.8 (23)
		U—O(1)—As	153.0 (15)	C(7)—As—C(13)	107.7 (23)
As—C(1)—C(2)	118.7 (38)	As—C(7)—C(8)	116.6 (36)	As—C(13)—C(14)	119.6 (32)
C(1)—C(2)—C(3)	119.6 (50)	C(7)—C(8)—C(9)	117.0 (45)	C(13)—C(14)—C(15)	125.0 (44)
C(2)—C(3)—C(4)	116.0 (63)	C(8)—C(9)—C(10)	123.6 (48)	C(14)—C(15)—C(16)	121.8 (58)
C(3)—C(4)—C(5)	123.0 (70)	C(9)—C(10)—C(11)	118.3 (47)	C(15)—C(16)—C(17)	113.7 (66)
C(4)—C(5)—C(6)	122.0 (65)	C(10)—C(11)—C(12)	121.0 (48)	C(16)—C(17)—C(18)	124.4 (78)
C(5)—C(6)—C(1)	113.6 (51)	C(11)—C(12)—C(7)	118.2 (46)	C(17)—C(18)—C(13)	125.5 (66)
C(6)—C(1)—C(2)	120.9 (52)	C(12)—C(7)—C(8)	120.8 (59)	C(18)—C(13)—C(14)	112.0 (52)

Table VI. Intramolecular bond lengths (Å) and their e.s.d.'s in parentheses (×10^2)

U—O(1)	2.36 (3)	As—O(1)	1.65 (4)	N—O(2)	1.34 (7)
U—O(2)	2.56 (4)	As—C(1)	1.88 (5)	N—O(3)	1.25 (7)
U—O(3)	2.60 (4)	As—C(7)	1.85 (5)	N—O(4)	1.16 (7)
U—O(5)	1.71 (3)	As—C(13)	1.89 (5)		
I Phenyl ring		II Phenyl ring		III Phenyl ring	
C(1)—C(2)	1.44 (8)	C(7)—C(8)	1.45 (8)	C(13)—C(14)	1.37 (7)
C(2)—C(3)	1.43 (10)	C(8)—C(9)	1.41 (8)	C(14)—C(15)	1.47 (7)
C(3)—C(4)	1.28 (10)	C(9)—C(10)	1.39 (7)	C(15)—C(16)	1.39 (11)
C(4)—C(5)	1.34 (11)	C(10)—C(11)	1.34 (8)	C(16)—C(17)	1.38 (13)
C(5)—C(6)	1.43 (10)	C(11)—C(12)	1.50 (9)	C(17)—C(18)	1.37 (12)
C(6)—C(1)	1.41 (9)	C(12)—C(7)	1.35 (7)	C(18)—C(13)	1.44 (10)

Mean value in the 18 C—C bonds = 1.40.

Table VII. Least-squares Planes

(a) Coefficients in AX+BY+CZ = D referred to the crystallographic axes

	A	B	C	D
Coordination plane (α) O(1), O(2), O(3), O′(1), O′(2), O′(3)	−7.3753	14.381	4.1539	0.000
Nitrate group (β) O(2), O(3), O(4), N	−0.7837	13.559	4.0828	−0.0298
I Phenyl ring (γ) C(1)—C(6)	−9.4664	10.041	5.6684	−0.9787
II Phenyl ring (δ) C(7)—C(12)	3.9335	18.026	−2.3785	3.6441
III Phenyl ring (ε) C(13)—C(18)	1.3888	7.5342	6.9587	2.1220

(b) Angles between the planes (°)

	α	γ	ε
β	4		
δ		79.3	65.8
ε		84.9	

(c) Deviations of the atoms from the planes (Å×10^3)

	α		β		γ		δ		ε
*As	188			*As	− 96	*As	205	*As	−206
O(1)	69			C(1)	− 47	C(7)	− 12	C(13)	− 11
O(2)	− 78	O(2)	0	C(2)	16	C(8)	− 29	C(14)	13
O(3)	74	O(3)	0	C(3)	7	C(9)	54	C(15)	14
O′(1)	− 69	O(4)	0	C(4)	2	C(10)	− 38	C(16)	− 44
O′(2)	78	N	1	C(5)	− 33	C(11)	− 2	C(17)	48
O′(3)	74			C(6)	55	C(12)	27	C(18)	− 20

* The arsenic atom is not included in the least-squares calculations.

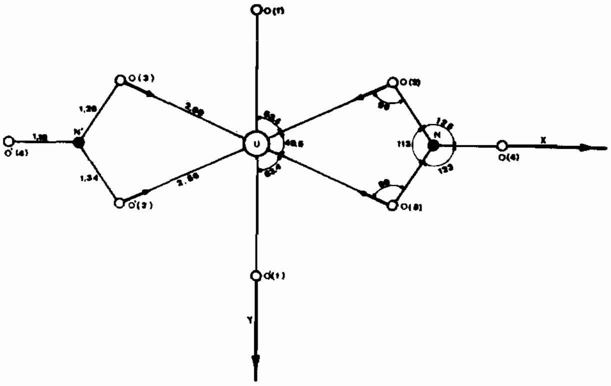
indicate that the normal covalent U—O bond lies between 2.35 and 2.40 Å. Therefore within the limits of the e.s.d'.s in the bonds and angles the chromophore UO_8 has D_{2h} symmetry.

The N—O bonds of the nitrate groups are not equivalent; those involving coordinated oxygen atoms are slightly longer (1.34, 1.25 Å) than the others (1.16 Å). In addition the angle O(2)—N—O(3) (111°) is considerably smaller than 120°. Therefore, the symmetry of the nitrate groups is lower than D_{3h}. The distorsion occurs with a decrease in the angle O(2)—N—O(3) and a lengthening of the bonds N—O(2), N—O(3) and U—O(2), U—O(3). Distorsion in the nitrate groups was also reported on the basis of the infrared spectra in the uranyl nitrate complexes[6] and was subsequentely confirmed by X-ray and neutron diffraction studies.[15] It is interesting to note that the mean value the of U–O–N angles is 99° which is very close to that observed in most oxygen compounds, such as water (104°). This suggests that the hybridization state of the oxygen atom is the same in these compounds. The previously noted distorsions could arise from the tendency of the oxygen to retain a bond angle close to 100°. In fact, assuming the D_{3h} symmetry for the nitrate group and the covalent value for the U–O bond length, the angle U–O–N would be ~90°, and there would not be any participation of the 2sA.O.'s of the oxygen.

A discussion of the hybridization state of the uranium on the basis of the bond angles cannot be carried out unequivocally owing to the many A.O.'s (5f, 6d, etc.) with almost equal energies.

However, because of the hexacoordination in a nearly equatorial plane commonly observed in the actinide coordination compounds, an important role may be played by the two A.O.'s $5f_{x(x^2-3y^2)}$ $(=\frac{1}{2}(f_{+3}+f_{-3}))$ and $5f_{y(3x^2-y^2)}$ $(=-{}^{i}/_{2}(f_{+3}-f_{-3}))$ having exactly six lobes in the plane. Moreover because of the nature of the ligands there is some distorsion from D_{6h} symmetry which to a first approximation (neglecting the $AsPh_3$ groups) is reduced to D_{2h}. The $5f_{x(x^2-3y^2)}$A.O. combines with σ_2–σ_3 of each nitrate group (where σ denotes the oxygen hybrid orbitals pointed towards uranium) and the $5f_{y(3x^2-y^2)}$ combines with $\sigma_2+\sigma_3$ (for the axis orientation and the nomenclature see Figure 3).

The overlap for the $5f_{x(x^2-3y^2)}$A.O. is at a maximum for a chelate angle of 60°. The overlap for the $5f_{y(3x^2-y^2)}$ is largest for a chelate angle of 0°. One would therefore expect the experimental value to be between these limits. In fact this value was 50°.



Figurc 3. Thc equatorial planc.

The As–O lenght, 1.65 Å, is similar to the distance 1 69 Å found in $HgCl_2.2Ph_3AsO$[16] and to 1.66 Å in the dimer of the same compound.[17] A value of 1.70 Å also was found in $Co(Ph_2CH_3AsO)_4(ClO_4)_2$.[18] This very short As–O distance can be ascribed to the strong π character of this bond. Similar bond shortening has been found in some P–O distances.[19]

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