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THE CRYSTAL STRUCTURE OF BROMO(TRIBROMOGERMYL)-2,2'-BIPYRIDINETRICARBONYLTUNGSTEN

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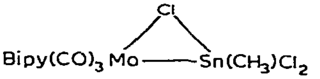
SUMMARY

The crystal structure of 2,2'-bipyridine$(CO)_3BrWGeBr_3$ has been determined, using three-dimensional counter data. The structure was refined by least squares to an R index of 0.10. The crystals are monoclinic, $a=8.62$, $b=16.15$, $c=13.58$ Å, $\beta=90.3°$, space group $P2_1/c$. The molecule contains $Bipy(CO)_3BrW$ and $GeBr_3$ residues connected by a W–Ge bond of length 2.608 Å. Unlike the situation in other similar molecules, the bromine attached to the tungsten does not bridge the W–Ge bond, and the geometry of the coordination of the heptacoordinate molybdenum is that of capped octahedron rather than capped trigonal prism.

INTRODUCTION

The geometry of ligand atoms about a central metal may often be predicted[1] with considerable accuracy for lower coordination numbers, but this is more difficult to do for coordination number seven. The three "ideal" heptacoordinate configurations, *viz.* the capped trigonal prism, the capped octahedron and the pentagonal bipyramid, do not differ greatly in energy, and it has been suggested[2] that because of this there may be no consistently adopted configuration for a particular molecule type. A molecule may even show different configurations in different physical states, as such influences as packing or solvent association energy may be sufficient to alter the energy balance, and similarly, quite subtle chemical differences between compounds may prove to be definitive.

A series of compounds has been described[3], of general formula $Y(CO)_3$-$MM'RX_3$, where Y is 2,2'-bipyridine(Bipy) or dithiohexane, M is tungsten or molybdenum, M' is tin or germanium, X is a halogen and R is either a halogen or an alkyl group. The IR spectra of these compounds in dichloromethane solution may show two distinct sets of three bands in the carbonyl stretching region, relative intensities of the two sets varying as Mo → W, Sn → Ge, Cl → Br → I, alkyl $M'X_3$ → $M'X_4$. Thus $Bipy(CO)_3MoSnCH_3Cl_3$ (I) showed bands of one set only, $Bipy(CO)_3WGeI_4$ (II) those of the other. Compounds intermediate in the series, *e.g.* $Bipy(CO)_3WGeBr_4$ (III), gave mixed spectra containing four or five resolvable bands. It appeared that the molybdenum or tungsten atom was heptacoordinate, and it was suggested that the spectral differences correspond to different coordination geometries, and that in the intermediate cases distinct isomers may co-exist in dichloromethane solution. Crystal structure analysis of (I) has shown[4] it to contain Bipy(CO)$_3$Mo and SnCH$_3$Cl$_2$ residues, linked by a direct Mo–Sn bond and also by a chlorine bridge



thus displaying seven-coordinate molybdenum and five-coordinate tin. The spectrum of (dithiohexane)WSnCH$_3$Cl$_3$ (IV) shows the same set of stretching frequencies, and the compound has essentially the same structure[5]. Attempts to determine the structure of compounds which show the alternative set, *viz.* (II) and its molybdenum analogue, were thwarted by the fact that the crystals are disordered[6]. Consequently the structure of the intermediate spectral type compound (III) has been studied, in the hope that it may indicate the nature of the alternative geometry.

EXPERIMENTAL

Deep red prismatic crystals of Bipy(CO)$_3$WGeBr$_4$ were supplied by Dr. W. A. G. Graham. These were monoclinic, $a=8.62\pm0.01$, $b=16.15\pm0.02$, $c=13.58\pm0.01$ Å, $\beta=90.3\pm0.2°$, $d_o=2.73$, $d_c=2.81$ g·cm^{-3} for 4 molecules per unit cell, space group $P2_1/c$. The cell parameters were obtained from precession photographs, taken with Cu-$K\alpha$ radiation.

Intensity data were collected using a PAILRED automated diffractometer, which employed crystal monochromated Mo-$K\alpha$ radiation. The procedure adopted has been described elsewhere[4]. Of 2900 reflections scanned, 1100 were deemed to be significantly above background ($\sigma(I)/I > 0.35$). No reflections were observable for $\sin\theta > 0.43$. The crystal was mounted about a, and was of dimensions 0.258 × 0.129 × 0.129 mm parallel to a, b and c respectively.

Structure determination and refinement

The tungsten and four of the other heavy atoms were readily located from a Patterson synthesis, and all remaining atoms from subsequent Fourier syntheses. Refinement was by full matrix least squares, assuming anisotropic thermal motion for the heavy atoms and isotropic motion for the light atoms. Atomic scattering factors were as in the International Tables[7], with real dispersion corrections for the tungsten and bromine atoms. In the later cycles correction was made for anomalous dispersion. The least squares weights were calculated assuming that $\sigma(I)=(I+t^2\cdot B+K\cdot I^2)^{\frac{1}{2}}$, where I is the intensity, t the ratio of scan time to background count time, B the total background count and K an internally optimised constant, taken as 0.06. The R index converged at 0.102, and intensities were then corrected for absorption, but this had little effect and the final value for R was 0.100.

RESULTS AND DISCUSSION

Atom coordinates are listed in Table 1, thermal parameters in Table 2, observed and calculated structure factors in Table 3. The molecule is shown in Fig. 1,

TABLE 1

ATOM COORDINATES

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
W	0.3249(2)	0.1983(1)	0.3478(2)	C(2)	0.138(7)	0.029(4)	0.585(4)
Ge	0.4270(6)	0.0816(4)	0.2360(4)	C(3)	0.013(6)	0.079(4)	0.625(4)
Br(1)	0.0683(6)	0.1476(4)	0.2669(5)	C(4)	−0.014(6)	0.157(4)	0.590(4)
Br(2)	0.3324(8)	0.0679(5)	0.0797(5)	C(5)	0.080(5)	0.184(3)	0.519(3)
Br(3)	0.4013(9)	−0.0482(4)	0.2992(6)	C(6)	0.061(4)	0.265(2)	0.479(3)
Br(4)	0.6893(7)	0.0848(5)	0.1979(6)	C(7)	−0.058(6)	0.318(3)	0.510(4)
O(1)	0.608(4)	0.119(2)	0.452(3)	C(8)	−0.078(6)	0.393(3)	0.463(4)
O(2)	0.564(5)	0.330(3)	0.411(3)	C(9)	0.023(6)	0.417(3)	0.390(4)
O(3)	0.428(5)	0.272(3)	0.148(3)	C(10)	0.148(7)	0.366(4)	0.356(4)
N(1)	0.206(5)	0.146(3)	0.477(3)	C(11)	0.504(6)	0.152(3)	0.401(4)
N(2)	0.164(5)	0.290(3)	0.407(3)	C(12)	0.469(6)	0.285(3)	0.389(4)
C(1)	0.240(6)	0.068(3)	0.515(4)	C(13)	0.385(6)	0.249(4)	0.226(4)

TABLE 2

THERMAL PARAMETERS (Å^2)

Anisotropic atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.026(1)	0.043(1)	0.057(2)	0.000(1)	0.001(1)	0.003(2)
Ge	0.031(3)	0.053(4)	0.052(4)	−0.002(3)	0.002(3)	0.002(3)
Br(1)	0.035(3)	0.075(5)	0.080(5)	−0.009(3)	−0.003(3)	−0.010(4)
Br(2)	0.070(5)	0.102(6)	0.093(6)	−0.008(4)	−0.007(4)	−0.007(5)
Br(3)	0.096(5)	0.062(5)	0.109(6)	0.011(4)	0.034(5)	0.012(4)
Br(4)	0.048(4)	0.136(7)	0.104(6)	0.004(4)	0.014(4)	−0.001(5)

Isotropic atom	B	Atom	B	Atom	B
O(1)	5.4(0.9)	C(2)	5.1(1.3)	C(8)	4.1(1.2)
O(2)	6.7(1.0)	C(3)	5.1(1.4)	C(9)	4.1(1.2)
O(3)	7.2(1.1)	C(4)	4.7(1.3)	C(10)	6.2(1.5)
N(1)	4.3(0.9)	C(5)	2.1(0.9)	C(11)	4.7(1.3)
N(2)	4.3(0.9)	C(6)	1.4(0.8)	C(12)	4.6(1.3)
C(1)	4.5(1.3)	C(7)	4.0(1.1)	C(13)	4.7(1.3)

and a stereodiagram of the structure in Fig. 2. Bond lengths and angles are listed in Table 4.

The molecule is essentially similar in structure to (I), in that the tungsten atom is seven-coordinate, with the bidentate Bipy, three carbonyls, a bromine atom and the $GeBr_3$ group as ligands. It differs in that the bromine atom attached to the tungsten is 3.31 Å from the germanium, and thus cannot be considered to be bonded to the germanium atom also. [By comparison, the corresponding Cl–Sn approach[4] in (I) is 2.805 Å.] It differs also in that the geometrical arrangement of the seven ligand atoms around the tungsten atom is not a capped octahedron, but closely approximates a

(continued p. 96)

TABLE 3

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

K	L	FO	FC
	H = 0		
0	8	400	403
0	10	847	681
1	1	688	587
1	4	619	658
1	5	772	769
1	6	1933	1162
1	7	1098	986
1	9	1871	1473
1	12	593	583
2	1	916	877
2	3	1563	1691
2	4	1770	1600
2	5	747	706
2	6	1741	1633
2	8	937	952
2	9	887	683
2	10	968	1069
2	11	797	881
3	1	1767	1106
3	3	1488	1433
3	4	1530	1608
3	6	606	670
3	7	1109	966
3	9	523	498
3	11	608	597
3	12	621	678
4	1	1215	1168
4	2	533	568
4	4	1417	1600
4	5	2611	2682
4	6	1337	1174
4	7	1162	1067
4	8	960	1263
5	1	1775	1845
5	3	3738	3014
5	4	1081	1009
5	5	774	717
5	6	1663	1388
5	7	710	657
5	8	1002	941
5	9	518	660
5	12	623	671
6	0	1117	1171
6	2	658	626
6	3	1170	1256
6	4	423	761
6	5	2138	1033
6	6	807	809
6	7	601	350
6	9	696	719
6	11	813	835
7	1	885	881
7	3	1703	1178
7	4	1117	1018
7	6	720	736
7	7	2118	2036
7	8	527	487
7	9	878	1090
7	12	527	501
8	0	1717	1102
8	1	1638	1818
8	3	821	811
8	4	1040	1005
8	5	766	666
8	6	682	632
9	2	1038	988
9	4	782	770
9	5	831	747
9	6	1207	1166
9	8	1136	1252
10	0	643	573
10	1	1266	1112
10	4	1126	1147
10	6	1016	1180
10	10	763	788
11	3	1696	1661
11	4	687	569
11	5	706	591
4	-8	683	809
4	9	678	866
4	-9	570	807
4	-11	116	817
5	1	1038	1010
5	-1	2166	2359
5	-2	2692	2607
5	3	1617	1441
5	-3	3663	3490
5	4	659	502
5	-4	669	617
5	5	3859	2774
5	-5	1666	1517
5	6	1173	1147
5	-6	368	319
5	7	569	716
5	-7	1178	1242
5	9	661	670
5	-11	513	706
6	0	1777	1780
6	1	1118	1113
6	2	698	646
6	-2	2358	2281
6	3	1206	1099
6	-3	1188	1269
6	4	2063	1895
6	-4	1109	1148
6	5	385	316
6	6	1421	1306
6	-6	370	603
6	7	1183	1169
6	-7	2073	1851
6	8	451	515
6	-8	1178	1106
6	11	682	769
6	-11	660	318
7	0	1119	1127
7	1	644	849
7	-1	1175	1115
7	2	700	683
7	-2	617	647
7	3	1630	1500
7	4	874	700
7	-4	808	864
7	5	1166	1216
7	-5	601	655
7	-6	1080	1074
7	7	471	705
7	-7	593	495
7	8	606	361
7	-10	686	608
7	11	510	561
7	-11	767	770
8	0	1878	1408
8	1	2761	2747
8	-1	1617	1631
8	2	2370	2279
8	3	2566	2294
8	4	1636	1618
8	-4	1657	1648
8	5	1030	1032
8	6	781	744
8	-7	696	716
8	8	767	856
8	-8	668	819
8	-9	880	786
9	0	1638	1646
9	1	1061	1019
9	2	812	476
9	-2	786	761
9	4	2051	1826
9	-5	897	881
9	6	817	610
9	-6	795	811
9	-7	667	296
9	8	782	842
9	10	608	617
9	-10	618	772
10	0	813	766
10	8	916	537
3	-12	688	673
3	1	761	713
3	-1	878	918
3	3	376	366
3	-3	1939	1916
3	4	670	671
3	-4	1071	960
3	5	1969	1868
3	-5	1963	1988
3	6	1916	1766
3	-6	1731	1650
3	7	1501	1431
3	-7	676	718
3	-8	1172	1212
4	0	730	701
4	1	1718	1817
4	-1	3783	3381
4	2	370	361
4	-2	1378	1350
4	3	2679	2778
4	-3	1863	1770
4	-4	678	319
4	5	662	510
4	-5	1140	1215
4	6	676	616
4	-6	862	733
4	-7	648	612
4	-8	800	868
4	9	1731	1460
4	-9	604	676
4	-10	579	513
4	-11	746	835
4	-13	765	677
5	0	811	868
5	1	3378	3164
5	3	808	744
5	-3	3372	2116
5	4	1068	1018
5	5	1681	1607
5	-5	1791	1608
5	6	1807	1719
5	-6	1711	1000
5	7	1734	1678
5	-7	886	656
5	8	653	878
5	-9	871	881
5	10	537	669
5	-11	450	782
5	12	813	688
5	-13	465	372
6	1	1031	1041
6	-1	3385	3336
6	2	433	601
6	-2	817	808
6	3	1321	1030
6	-3	814	703
6	-4	676	607
6	5	705	786
6	-5	1005	900
6	-6	918	708
6	7	818	871
6	-7	1422	1324
6	8	576	666
6	9	672	881
6	-11	858	831
6	-13	556	540
7	1	3401	3671
7	-1	2066	1086
7	2	470	447
7	-2	1198	1360
7	3	826	766
7	-3	667	569
7	4	687	669
7	-4	1787	1458
7	5	509	482
7	6	863	817
7	-6	976	976
7	-7	818	791
7	-8	616	611
7	-9	658	646
1	8	749	910
1	-8	2107	2016
1	-12	685	637
2	2	1067	1146
2	-3	1013	1157
2	-4	1001	1142
2	-5	1317	1360
2	6	1607	1470
2	-6	1141	1217
2	-7	646	797
2	-8	950	868
2	10	560	751
2	-10	1376	1226
2	-11	571	668
3	0	651	639
3	1	1576	1516
3	-1	1743	1169
3	2	961	810
3	-2	1319	1676
3	3	2444	2333
3	-3	1215	1216
3	-4	1369	1361
3	5	630	378
3	-5	1035	1036
3	6	606	711
3	-6	817	818
3	-7	1670	1869
3	8	696	917
3	-9	771	673
3	11	567	527
4	1	885	887
4	-1	1866	1873
4	-3	940	733
4	-4	910	656
4	5	1085	1002
4	-5	667	590
4	6	850	855
4	7	988	1069
4	-7	761	773
4	-9	2144	1880
4	-11	369	389
5	1	667	607
5	-1	2370	2098
5	2	1660	1517
5	3	1563	1673
5	-3	2868	2853
5	4	703	636
5	7	880	862
5	-7	657	667
5	-8	699	496
5	9	781	1061
5	-13	605	577
6	0	529	501
6	1	1561	1627
6	-1	1140	1167
6	-2	661	680
6	-3	2116	1079
6	4	561	590
6	-4	581	576
6	5	666	695
6	-5	1058	1081
6	6	1030	1030
6	-7	821	844
6	-8	1276	1008
6	-10	1069	911
6	11	609	758
6	-12	570	588
7	0	1079	1084
7	-2	1221	1001
7	3	1566	1366
7	-3	634	581
7	4	801	850
7	-4	1079	1069
7	5	606	588
7	-6	615	537
7	7	1331	1278
7	-7	1190	1958
7	-8	841	718
8	0	1058	1108
8	1	1085	1091
3	-8	1365	1717
3	-10	677	578
3	-12	597	306
3	0	1168	1316
3	1	2051	2046
3	-1	2278	2605
3	2	490	570
3	-2	1531	1890
3	3	399	400
3	-3	688	715
3	-4	674	570
3	5	903	872
3	-5	1000	1018
3	6	810	960
3	-6	805	783
3	-7	678	554
3	8	850	889
3	-9	695	611
3	10	518	719
3	-11	700	748
4	0	357	303
4	1	1735	1747
4	-1	651	603
4	3	1258	1176
4	4	741	766
4	5	1510	1673
4	6	413	873
4	-6	577	610
4	7	1227	1570
4	-7	1078	919
4	8	578	917
4	-8	867	850
4	-9	812	776
5	0	697	687
5	1	1976	1803
5	-1	2869	2896
5	2	767	767
5	-2	1967	1976
5	-3	1075	1032
5	4	567	880
5	-4	1034	1017
5	5	1332	1367
5	-5	1331	1284
5	-6	867	860
5	-7	796	570
5	-8	969	873
5	9	593	863
5	-9	677	813
6	1	750	748
6	-1	766	776
6	2	400	606
6	-2	688	667
6	3	886	800
6	-3	1017	1016
6	4	670	655
6	-5	878	707
6	6	873	818
6	7	905	1168
6	-7	1295	1065
6	-8	585	381
6	-9	700	850
7	0	2091	1076
7	1	578	668
7	2	1150	1086
7	-2	1268	1133
7	3	2666	2656
7	-3	1693	1303
7	-4	660	760
7	5	1361	1627
7	-5	1511	1389
7	-6	918	867
7	-7	966	876
8	0	761	681
8	1	1099	1013
8	2	1172	1060
8	-2	596	475
8	3	816	665
8	-3	865	765
8	4	793	683
8	-4	1274	1111
3	-9	609	513
3	-10	885	713
4	-1	1700	1276
4	2	742	735
4	3	747	666
4	-3	896	547
4	4	644	574
4	-5	1087	1116
4	7	1148	943
4	-7	614	667
4	9	1815	1596
4	11	816	643
4	-11	1056	766
4	-12	870	708
5	1	2916	2311
5	-1	355	286
5	3	1615	1380
5	-3	768	767
5	4	644	298
5	5	870	603
5	-5	1018	920
5	6	852	636
5	7	1000	906
5	-9	1675	1758
6	0	686	580
6	1	870	599
6	-1	1679	1650
6	-2	948	918
6	3	1605	1477
6	-3	675	699
6	4	606	866
6	5	1303	1182
6	-5	517	640
6	-7	1761	1116
6	8	1098	967
6	10	833	716
6	-11	864	571
7	0	1275	1017
7	1	1069	1961
7	-1	631	661
7	2	1077	987
7	-2	877	618
7	-3	888	814
7	-6	1786	1710
7	5	706	576
7	6	816	642
7	7	1717	967
7	-7	801	678
7	-9	764	609
7	-10	808	603
8	0	607	576
8	-1	640	714
8	2	964	670
8	3	1116	1160
8	4	1780	1519
8	5	1706	1112
8	-5	510	698
8	6	662	570
8	-6	877	688
8	-7	868	503
8	-10	701	560
9	0	708	772
9	1	503	673
9	2	838	680
9	3	676	613
9	-6	565	876
9	6	1379	1073
9	8	866	670
9	-8	803	610
10	0	677	618
10	2	773	677
10	-3	1200	1170
10	3	858	766
10	4	1330	1083
10	6	813	748
10	-6	1100	816
10	-8	619	668
11	0	1178	1065
11	1	686	687
11	2	1670	1372
6	5	666	956
6	-5	1062	950
6	6	778	678
7	2	777	656
7	-3	1017	955
7	3	868	770
7	-3	907	890
7	4	838	770
7	-4	569	371
7	7	979	686
8	0	1108	1093
8	1	667	611
8	-3	533	635
8	4	691	696
8	-4	1074	1007
8	-5	719	733
8	5	588	599
9	0	678	678
9	-1	649	976
9	2	906	635
9	-2	1090	1018
9	4	679	866
9	-4	709	683
10	0	1147	1180
10	3	1769	1050
10	-3	633	577
10	-4	964	876
11	-1	721	860
11	3	1018	811
11	-3	1113	969
11	5	688	806
11	-5	766	673
	H = 2		
0	3	910	886
0	-2	1476	1604
0	4	997	1059
0	-6	866	659
0	8	967	757
0	-8	968	953
1	-1	651	597
1	1	806	870
1	-3	617	519
1	4	1745	1163
1	-6	671	526
1	5	619	578
1	6	806	868
1	-8	518	769
1	-9	756	619
2	2	1636	1703
2	-2	863	651
2	3	716	797
2	-3	1333	1396
2	4	714	754
2	6	586	431
2	-6	676	780
2	-8	666	605
2	9	514	765
3	1	696	677
3	-1	1107	1291
3	3	701	527
3	-6	580	766
3	4	1033	838
3	-5	676	683
3	-6	1088	1136
3	7	658	657
4	1	1676	1545
4	3	1300	1351
4	-5	667	666
4	7	630	695
4	-7	1185	1187
5	1	1117	1105
5	-1	1158	1251
5	5	977	750
5	-5	1366	1361
5	-7	606	791
6	0	863	805
6	-1	606	696
6	3	1190	1191

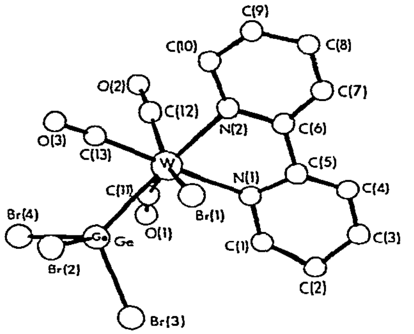


Fig. 1. The Bipy(CO)$_3$BrGeBr$_3$ molecule.

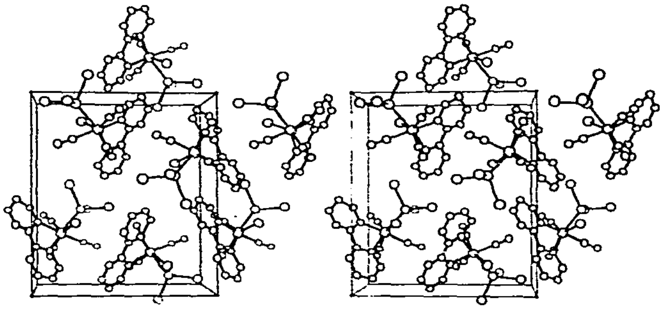


Fig. 2. A stereo-diagram of the structure.

capped trigonal prism, with the bromine atom, Br(1), above the centre of one of the square faces, as shown in Fig. 3. The bromine is more or less equidistant from the four atoms which comprise the capped face, the separations ranging from Br(1)–W(1) at 3.08 Å to Br(1)–Ge at 3.31 Å. The major distortions from regularity of the prism appear to be associated with the presence of the capping bromine, and with the fact that the W–Ge bond, at 2.608 Å is considerably longer than the tungsten-light atom bonds. Thus the edge N(2)–C(13) is 3.19 Å whereas the edge N(2)–C(12) is 2.64 Å, and the prism angles about a vertex which ideally should be of 60°, 90° and 90°, are 44°, 69°, 73° about the germanium and 54°, 100°, 105° about C(13).

The W–Ge bond length of 2.608(6) Å may be compared with the W–Sn bond

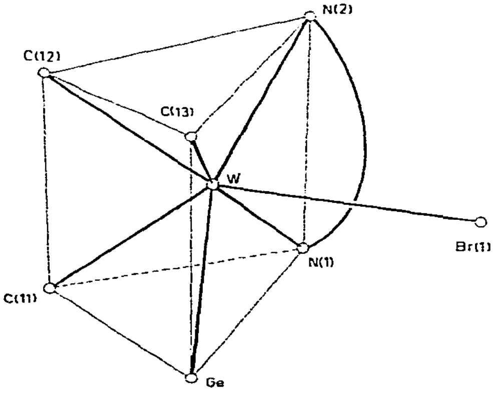


Fig. 3. The capped trigonal prismatic arrangement of ligand atoms about the tungsten.

length of 2.759(3) Å in (IV). The germanium covalent radius has been estimated[7] at 1.22 Å, although in view of the fact that the Ge–Br bond length in GeHBr$_3$ has been reported[8] as 2.298(3) Å, a value of 1.16 Å might be more appropriate. In either case the germanium radius appears to be much smaller than that of tin[9], 1.39 Å, and the shorter length of the W–Ge bond is thus accounted for by the decreased size of the Group IV metal. A value of 1.58 Å for the radius of tungsten has been estimated[10] from the tung-

TABLE 4

BOND LENGTHS (Å) AND BOND ANGLES (°)

W–Ge	2.608(6)	N(2)–C(10)	1.44(8)
W–Br(1)	2.603(6)	C(1)–C(2)	1.45(8)
W–C(11)	1.86(6)	C(2)–C(3)	1.45(8)
W–C(12)	1.97(6)	C(3)–C(4)	1.39(8)
W–C(13)	1.92(6)	C(4)–C(5)	1.35(7)
W–N(1)	2.21(4)	C(5)–C(6)	1.44(6)
W–N(2)	2.20(4)	C(6)–C(7)	1.41(6)
Ge–Br(2)	2.280(9)	C(7)–C(8)	1.41(8)
Ge–Br(3)	2.319(9)	C(8)–C(9)	1.38(8)
Ge–Br(4)	2.322(8)	C(9)–C(10)	1.45(8)
N(1)–C(1)	1.41(7)	C(11)–O(1)	1.26(7)
N(1)–C(5)	1.39(6)	C(12)–O(2)	1.14(7)
N(2)–C(10)	1.38(6)	C(13)–O(3)	1.19(7)
Ge–W–Br(1)	78.8(2)	Br(2)–Ge–Br(3)	102.6(4)
Ge–W–C(11)	69(2)	Br(2)–Ge–Br(4)	98.0(3)
Ge–W–C(12)	119(2)	Br(3)–Ge–Br(4)	101.4(3)
Ge–W–C(13)	74(2)	W–C(11)–O(1)	168(5)
Ge–W–N(1)	109(1)	W–C(12)–O(2)	173(5)
Ge–W–N(2)	159(1)	W–C(13)–O(3)	173(5)
Br(1)–W–C(11)	137(2)	W–N(1)–C(1)	124(3)
Br(1)–W–C(12)	152(2)	W–N(1)–C(5)	121(3)
Br(1)–W–C(13)	91(2)	C(1)–N(1)–C(5)	115(4)
Br(1)–W–N(1)	79(1)	W–N(2)–C(10)	119(3)
Br(1)–W–N(2)	81(1)	W–N(2)–C(6)	117(3)
C(11)–W–C(12)	71(2)	C(6)–N(2)–C(10)	123(4)
C(11)–W–C(13)	106(3)	C(2)–C(1)–N(1)	121(5)
C(11)–W–N(1)	85(2)	C(1)–C(2)–C(3)	117(5)
C(11)–W–N(2)	132(2)	C(2)–C(3)–C(4)	121(5)
C(12)–W–C(13)	76(2)	C(3)–C(4)–C(5)	117(5)
C(12)–W–N(1)	111(2)	C(4)–C(5)–C(6)	121(4)
C(12)–W–N(2)	78(2)	C(4)–C(5)–N(1)	128(4)
C(13)–W–N(1)	168(2)	C(6)–C(5)–N(1)	111(4)
C(13)–W–N(2)	101(2)	C(5)–C(6)–C(7)	123(4)
N(1)–W–N(2)	72(2)	C(5)–C(6)–N(2)	118(4)
W–Ge–Br(1)	50.5(2)	C(7)–C(6)–N(2)	120(4)
W–Ge–Br(2)	119.7(3)	C(6)–C(7)–C(8)	120(4)
W–Ge–Br(3)	115.7(3)	C(7)–C(8)–C(9)	120(5)
W–Ge–Br(4)	116.4(3)	C(8)–C(9)–C(10)	122(5)
		C(9)–C(10)–N(2)	115(5)

sten-carbonyl bond length of 1.96 Å in (π-C_5H_5)$C_6H_5(CO)_3W$, and this is in fair agreement with the 1.61 Å which may be deduced from the observations that the W–Sn and Mo–Sn bond lengths are near identical in (IV) and (I) respectively, and that 3.22 Å is the length of a Mo–Mo single bond[11]. On these estimates the calculated W–Ge single bond length would be in the range 2.74–2.83 Å, and although there are no other experimental data on this bond for comparison, the observed value of 2.608 Å must indicate that in the present compound the bond order is greater than one.

The coordination about the germanium is approximately tetrahedral, with the angles somewhat distorted by the greater repulsions associated with the tungsten atom. The average Br–Ge–Br angle is thus 100°, compared with the average W–Ge–Br of 117°. In fact the range of angle about the germanium, 98–120°, is smaller than the range for the corresponding angles in (IV), 97–124°, and in (I), 95–127°, but much less so than might have been expected in view of the fact that in the latter two molecules there is an additional close approaching halogen, and that the coordination about the tin atom was then described as distorted trigonal bipyramidal. Consideration of inter-ligand angles would thus seem a weak basis on which to justify the latter description. It may be more significant that in (I), in which compound the fifth ligand makes the closest approach to the tin, the "axial" Sn–Cl bond is very significantly longer than the "equatorial" Sn–Cl bond, whereas in the present molecule, the three Ge–Br bond lengths are equal, within error, and none differs significantly from the value observed[8] in $HGeBr_3$.

It is instructive to consider the geometry of the coordination about the tungsten atom in this compound, and the corresponding atoms in (I) and (II), in terms of tetragonal base–trigonal base geometry. A capped trigonal prism can be described as a polygon in which four vertices are those of a plane quadrilateral face, and the remaining three of a parallel triangular face, oriented as in Fig. 4(i). The capped octahedron, can, with some symmetrical distortion, be described on a similar basis with the two faces relatively rotated by 45°, as in Fig. 4(ii)[12]. The geometries of the two isomers of $S_2Fe_3(CO)_9$, in which the iron is heptacoordinate, have been shown[12] to differ in just this way. The ligand distribution, viewed as for Fig. 4, is shown in Fig. 5 for the present compound and for (I), and thus for the former Ge, C(11), C(12) and C(13) comprise the tetragonal base, and N(1), N(2) and Br(1) the trigonal. It

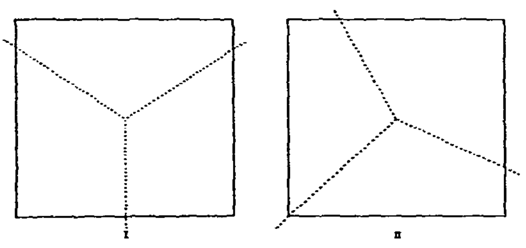


Fig. 4. Tetragonal base–trigonal base geometries.

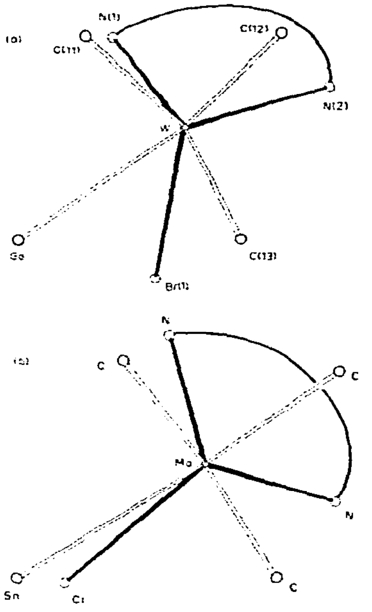


Fig. 5. (a). The arrangement of ligand atoms in $Bipy(CO)_3BrGeBr_3$, viewed down the tetragonal base–trigonal base 'axis'. (b) The corresponding arrangement in $Bipy(CO)_3ClSnCH_3Cl_2$.

appears that the determining factor controlling the relative rotation of the two, and thus the coordination geometry, could well be the strength of the attraction between the Group IV metal and the halogen, and as the variations in molecular composition which have been observed to affect the carbonyl stretching frequencies in dichloromethane solution could also be reflecting just this attraction, it is suggested that this is the nature of the isomerism postulated[3].

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