Crystal Structure of Tetraethylammonium Tetracarbonyltribromotungstate(II)

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Summary The tetracarbonyltribromotungstate(II) anion has C_{3v} (capped octahedral) symmetry.

As stable seven-co-ordinate mononuclear complexes are predominantly chelate species, configuration geometries obtained with monodentate ligands are of considerable interest,[1,2] particularly as any chelate can have a considerable distorting effect on the stereochemistry of the co-ordination sphere. We have determined the crystal structure of one such monodentate compound, the $[W(CO)_4Br_3]$ anion in the tetraethylammonium salt. *Crystal Data:* $C_{12}H_{20}NBr_3WO_4$, $M = 655{\cdot}9$, $a = 20{\cdot}109(14)$, $b = 9{\cdot}693(10)$, $c = 10{\cdot}396(9)$ Å, $Z = 4$, $U = 2026{\cdot}3$ Å^3, orthorhombic, space group *Pnma*.

The intensities of 743 independent reflections above background (with $2\theta < 40°$) were measured on a G.E. XRD 5 manual diffractometer. The structure was solved by Patterson and Fourier methods and refined (W, Br anisotropic, N, C, O isotropic) to R 0·063. Both ions have high thermal motion (average B values are 7 for the anion and 10 for the cation), and the tetraethylammonium ions are disordered about the mirror planes in the unit cell.† However, the anion shows no sign of disorder and structural details are shown in the Figure (mean standard deviations are W–Br 0·004, W–C 0·06, C–O 0·07 Å). The W–Br and

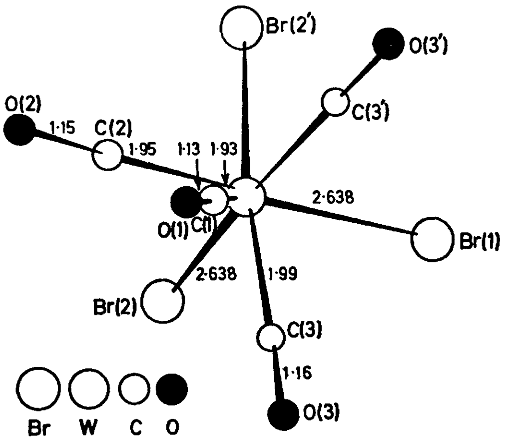

FIGURE. *The tetracarbonyltribromotungstate*(II) *anion. Primed atoms are related to unprimed atoms by the mirror plane.*

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† Refinements of the structure in $Pn2_1a$ were unsuccessful.

W–C–O dimensions (see Figure) are similar to those found [W–Br 2·65(1), W–C 1·99(4), C–O 1·17(5) Å] in the seven-co-ordinate molecule dibromotricarbonylbis[bis(diphenylarsino)methane]tungsten(II).[3] Atoms W(1), Br(1), C(1), O(1), C(2), O(2) lie on the mirror planes in the unit cell. The anion has C_{3v} symmetry within experimental error, the tungsten atom having the (1:3:3) capped octahedral environment. Of the three types of atom (L) in the co-ordination sphere, C(1) occupies the unique capping position, while the remaining three carbon atoms (designated C_c) make up the capped face and the three bromine atoms (Br_u) the uncapped face. Average dimensions found in the polyhedron are given in the Table.

TABLE

L–W–L type	Number in polyhedron	Mean angle[a] (°)	L · · · L (Å)
C(1)–W–C_c	3	74·1	2·35
C(1)–W–Br_u	3	125·5	4·14
C_c–W–C_c	3	112·8	3·24
Br_u–W–Br_u	3	89·6	3·72
$(C_c\text{–W–}Br_u)_{trans}$	3	160·4	4·52
$(C_c\text{–W–}Br_u)_{cis}$	6	79·6	2·90

[a] Mean standard deviations: C–W–C 2·0, C–W–Br 1·4, Br–W–Br 0·1°.

Calculations of the relative coulombic ligand–ligand repulsions for polyhedra formed with ML_7 species have shown[4] that the pentagonal bipyramid (D_{5h}) and the capped octahedron (C_{3v}) are the two most favoured, followed by the tetragonal base, trigonal base (C_s), and the capped trigonal prism (C_{2v}). Variations in this stereochemical order of preference for mixed species can be ascribed to the nature of the constituent ligands. For example, in the present compound, Br · · · Br repulsions are of predominant importance with (W–Br)/(Br · · · Br) distance ratios of 0·71 which cannot be fitted into either the D_{5h} or the C_{2v} polyhedron. Also the carbonyl groups, as strong π acceptors, prefer mutually *cis* positions, thus avoiding competition for the metal d_π electrons. This condition is best satisfied in the C_{3v} and C_s polyhedra where no C–W–C angle need be $>115°$. The Br · · · C repulsions will be less in the C_{3v} species than in the C_s species. The capped octahedral structure found for the $[W(CO)_4Br_3]$ anion could therefore have been predicted. This is the highest possible symmetry available to the anion. Crystal structures of seven-co-ordinate tungsten(II) and molybdenum(II) complexes containing bulky phosphorus or arsenic ligands show metal atoms in distorted capped octahedral environments[3,5,6] which are based on that found in the present anion.

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[1] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3626.
[2] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.
[3] M. G. B. Drew, A. W. Johans, A. P. Wolters, and I. B. Tomkins, *Chem. Comm.*, 1971, 819.
[4] R. B. King, *J. Amer. Chem. Soc.*, 1970, **92**, 6455.
[5] M. G. B. Drew, *J. C. S. Dalton*, 1972, 626.
[6] M. G. B. Drew, *J. C. S. Dalton*, in the press.