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The Crystal Structure of Protactinium Oxytribromide

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Protactinium oxytribromide, $PaOBr_3$, is monoclinic, $C2/m$, with $a=16{\cdot}911$ (2), $b=3{\cdot}871$ (3), $c=9{\cdot}334$ (7) Å and $\beta=113{\cdot}67$ (6)°, $Z=4$. The structure, solved from photographic data, has been refined in projection, as all the atoms lie on mirror planes, to $R=0{\cdot}066$. The metal coordination is sevenfold, approximating to pentagonal bipyramidal geometry, with bridging oxygen and bromine atoms giving rise to infinite chains parallel to [010]. The oxygen environment is unusual in that it links three protactinium atoms. The chain structure is similar to that reported for $Cs_xUO_3Cl_x$ ($x\sim0{\cdot}9$), and our compound should thus be systematically named catena-μ-bromo-μ_3-oxo-dibromoprotactinium(V). The method of choosing between the possible space groups $C2$, Cm, and $C2/m$ is discussed.

Introduction

As reported briefly before (Brown, Petcher & Smith, 1968) we were fortunate in obtaining a batch of crystals of this highly intractable compound, which is usually obtained only in a microcrystalline form. In spite of repeated attempts we have been unable to repeat the crystallization and we know of no other preparation of protactinium oxytribromide in large enough crystals for single-crystal diffraction studies. Most of the crystals of this batch were twinned or plastically deformed, but we were able to collect rather poorish X-ray data from one crystal. Because of the small likelihood of other crystals becoming available, we now present the best analysis we have been able to make of the data we obtained.

Experimental

Protactinium oxytribromide is obtained along with the pentabromide in the bromination of protactinium pentoxide with carbon and bromine (Brown & Jones, 1966); the pentabromide is removed by vacuum sublimation at 250 to 300°C, the oxytribromide normally being involatile under these conditions. Prolonged heating or higher temperatures result in the disproportionation of the oxytribromide into the pentabromide and the dioxybromide, PaO_2Br. On one occasion, during the purification of a batch of the pentabromide, some sizable yellow needles of the oxytribromide were obtained.

The unit cell was found to be monoclinic and the dimensions above were obtained by least-squares refinement from Debye–Scherrer powder patterns taken with nickel-filtered copper $K\alpha$ radiation (λ taken as 1·54178 Å). Zirconium-filtered molybdenum X-rays (λ taken as 0·7107 Å) were used to collect multiple-film Weissenberg photographs of reciprocal layers $h0l$ to $h3l$. The extremely high toxicity of protactinium compounds requires that the crystal be contained within a capillary, and this, as well as the shape of the crystal, prevented us from getting any correlating data. We had no precession camera for radioactive work. Systematic absences (hkl, $h+k=2n+1$) are compatible with the space groups $C2$, Cm, and $C2/m$. The density of the crystals could not be measured, though they were observed to sink in bromobenzene ($\varrho=3{\cdot}5$ g cm^{-3}). We assume $Z=4$, which gives $\varrho_{calc}=5{\cdot}78$ g cm^{-3}. 266 independent reflexions were measured visually and corrected for Lorentz, polarization, and absorption effects, the last by a Gaussian integration procedure following Busing & Levy (1957). $\mu=320$ cm^{-1}. The layers were scaled together initially on the basis of exposure times; at a later stage layer scale factors were included in the refinement. Unit weights were used throughout.

The structure was solved by Patterson and difference Fourier methods, but difficulties in trying to refine it were not resolved by the static disorder model we reported earlier.

Eventually we adopted the following reasoning. If the true space group contains mirror planes (Cm or $C2/m$) it follows from the short b dimension that all atoms must lie on them, and in that case all the structure factors are independent of k. Nevertheless, because of the C-centring, $k=2n$ and $k=2n+1$ reflexions form separate sets, but marked similarities between the $h0l$ and $h2l$ films and between the $h1l$ and $h3l$ were noted. To test this possibility the measured intensities were corrected for the variation of f with θ (using f values to adjust to $\theta=0$) and all pairs of corresponding reflexions were compared. The overall correlation coefficient (for $h0l$ with $h2l$ and $h1l$ with $h3l$) was found to be 0·91. As we were hoping for a final R value in the region of 0·05 to 0·10, we concluded that this correlation coefficient implies that any deviations from true mirror

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symmetry are not significantly greater than the expected experimental errors. From this point we assume that the space group is *Cm* or *C*2/*m*, and we are therefore able to discard the *h*2*l* and *h*3*l* reflexions, which are less accurate than those in the lower layers as evidenced by the appearance of the films, without any loss of information.

The *h*1*l* reflexions were also (from the appearance of the films) reckoned to be less accurate than the zero-layer ones. They are necessary, however, to distinguish which atoms lie on the $y=0$ mirror plane and which on $y=0{\cdot}5$. One atom may be placed arbitrarily (by choice of origin) and we accordingly placed the protactinium at $x=0{\cdot}19$ and $z=0{\cdot}31$ on $y=0$. In projection, the oxygen and Br(3) lie too close to the Pa to be in the same plane and they must therefore be placed on $y=0{\cdot}5$. There remain Br(1) and Br(2) which may lie on $y=0$ or 0·5. The four resulting models were each refined to convergence by using the *h*0*l* and *h*1*l* reflexions together. In every case a bromine at $y=0{\cdot}5$ refined to a high *B* value (12 to 19 Å^2) whereas a bromine at $y=0$ gave a more realistic value of about 4 Å^2. The *R* values for the models containing bromine at $y=0{\cdot}5$ were all higher (0·21 to 0·28) than that for the model with both bromines at $y=0$ (0·18). We conclude that this last model, which is the original one refined in *C*2, is correct, and, having so concluded, we now have no further use for the *h*1*l* data. (These are less accurate than the *h*0*l*, and the latter are sufficiently numerous for the refinement of the few structural parameters required.) The oxygen parameters were not included in these refinements.

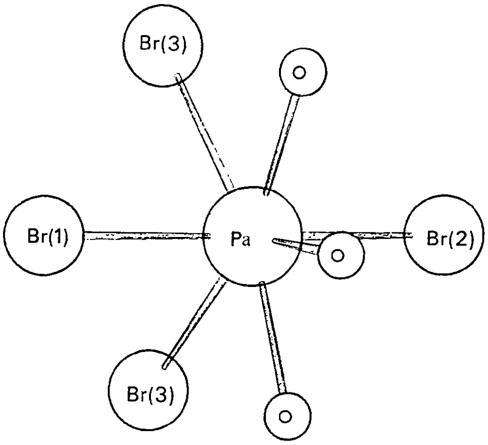

Fig. 1. Protactinium coordination.

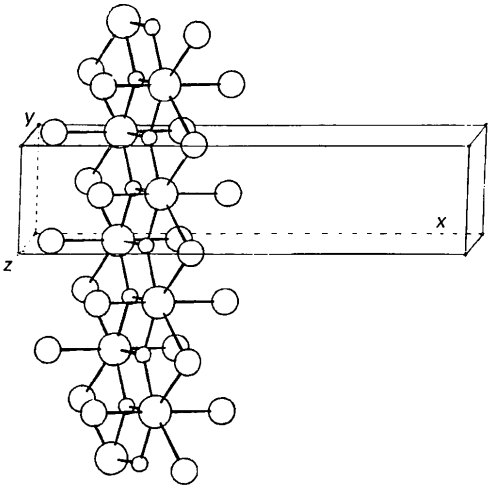

Fig. 2. The double chain structure.

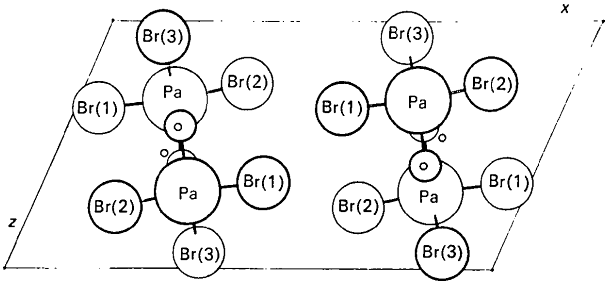

Fig. 3. Projection of the structure parallel to [010]. The atoms with bold outlines are at $y=0{\cdot}5$; the others at $y=0$.

We now come to the choice between the remaining space groups, *Cm* and *C*2/*m*. In *Cm* we have two independent protactinium atoms and their thermal vibration parameters become widely disparate upon refinement (one goes to about 0·5 and the other to above 10). Successful refinement could be achieved only by constraining the thermal parameters of the protactinium atoms to remain equal one to another, and likewise also for the pairs of bromine atoms related by the pseudo inversion centre. By this means refinements with isotropic vibrational parameters for all atoms were carried to convergence in *Cm* and *C*2/*m* with resultant *R* values of 0·0937 and 0·0952 respectively. These lead (Hamilton, 1965) to rejection at more than 0·5 probability of the hypothesis that the true symmetry is *Cm*.

We next considered the question of anisotropic vibration. As we had originally no independent method of scaling the layers together, we never had the option of determining β_{22}'s anyway, and have not lost this in rejecting the non-zero level data. But anisotropy of vibration in the *xz* plane can still be considered. A refinement in which the vibrations of all atoms (except oxygen) were allowed to be anisotropic, reduced the *R* value from 0·0952 to 0·0840, indicating the truth of this hypothesis at 95% probability. Examination of the resulting thermal ellipsoids showed that only that of Br(1) differed substantially from a sphere. Accordingly a further refinement in which the Br(1) vibrations only were allowed to be anisotropic was run to convergence. The *R* value test showed that this hypothesis is confirmed at greater than 99·5% probability but the further hypothesis that the other bromines and the protactinium vibrate anisotropically may then be rejected with 99·5% confidence.

Next the oxygen parameters were included in the refinement which was carried to a final *R* value of

0·066. Anisotropic vibrational parameters for the oxygen could not be refined. In the final cycle all parameter shifts were less than 0·1 of the corresponding e.s.d.'s and a final difference Fourier synthesis showed only small irregular peaks of a maximum height of 2 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The anomalous dispersion corrections for protactinium ($\Delta f' = -15{\cdot}75$ and $\Delta f'' = 13{\cdot}65$) were interpolated from Roof's (1961) values for thorium and uranium. The value of μ_a for protactinium (4523×10^{-23} cm^2) was similarly obtained from Roof (1959). The final positional and vibrational parameters are shown in Table 1 and the observed and calculated structure factors are listed in Table 2. The structure is illustrated in Figs. 1 to 3 and the bond lengths and angles are listed in Table 3.

Table 1. *Positional and vibrational parameters*

Estimated standard deviations in parentheses refer to the last quoted significant figure.

	x/a	y/b	z/c	B (Å^2)
Pa	0·1960 (6)	0·0	0·3151 (9)	0·84 (20)
Br(1)	0·0479 (14)	0·0	0·3503 (29)	*
Br(2)	0·3300 (17)	0·0	0·2495 (28)	5·03 (77)
Br(3)	0·1169 (15)	0·5	0·0659 (25)	3·93 (64)
O	0·231 (8)	0·5	0·421 (15)	2·28 (306)

* The temperature factor used for Br(1) was $\exp\{-[0{\cdot}0016\,(9)h^2 + 0{\cdot}0249k^2 + 0{\cdot}0739\,(48)l^2 + 0{\cdot}0088\,(32)hl]\}$.

Table 3. *Principal bond lengths* (Å) *and angles* (°)

Pa–Br(1)	2·65 (2)	O——Pa–O	64·6 (40)
Pa–Br(2)	2·57 (2)	O——Pa–Br(3)	73·7 (30)
Pa–2Br(3)	2·91 (2)	Br(3)–Pa–Br(3)	83·5 (6)
Pa–O	2·27 (11)	Br(1)–Pa–Br(2)	173·9 (7)
Pa–2O	2·14 (11)		

Discussion

The Pa–Br bond lengths are very slightly, but not significantly, longer than those found in β-PaBr$_5$ [2·85 to 2·86 Å bridging; 2·54 to 2·60 Å terminal: Brown, Petcher & Smith (1969)]. The coordination about the protactinium is, as in PaCl$_5$ (Dodge, Smith, Johnson & Elson, 1967), a pentagonal bipyramid, the apical atoms Br(1) and Br(2) being the only non-bridging ones. The bridging atoms lie very close to the least-squares plane through them (mean deviation 0·06 Å) and the protactinium atom lies within 0·03 Å of this plane, the equation of which is

$$0{\cdot}98643X - 0{\cdot}16416Z - 1{\cdot}6334 = 0$$

Table 2. *Observed and calculated structure factors*

h	l	F_o	F_c	α_c
0	2	122·8	122·9	−2·968
0	3	171·0	176·4	0·172
0	5	98·9	100·1	−2·897
0	6	43·2	35·9	0·448
0	8	74·1	73·0	−2·827
0	9	38·6	26·2	0·398
2	−9	69·4	73·5	−2·833
2	−7	36·7	39·4	0·277
2	−4	90·8	89·5	0·209
2	2	133·4	132·5	0·206
2	3	116·9	115·6	−2·980
2	4	146·5	142·2	−2·975
2	5	94·4	95·4	0·268
2	7	88·3	91·5	−2·892
2	8	61·1	58·0	0·334
4	−9	91·2	90·5	0·276
4	−7	63·8	66·8	−2·824
4	−6	128·7	127·1	0·206
4	−5	63·2	56·5	0·166
4	−4	112·6	110·8	−2·909
4	−3	45·3	41·9	0·299
4	2	82·9	85·8	−2·893
4	7	67·5	89·8	0·283
6	−10	66·6	64·5	0·343
6	−7	85·1	92·1	0·278
6	−6	44·9	43·7	−2·947
6	−5	145·6	144·1	−2·954
6	−4	123·2	125·3	0·205
6	−2	267·6	267·2	−3·000
6	−1	123·7	103·0	0·177
6	0	82·6	65·7	0·208
6	1	134·9	132·2	−2·928
6	2	57·3	60·1	0·186
6	3	74·3	73·2	0·261
6	4	25·9	40·0	−2·675
6	5	38·6	33·7	0·147
6	6	55·3	60·8	0·332
8	−10	72·3	47·6	−2·765
8	−8	35·1	36·0	0·514
8	−6	60·8	59·2	−2·923
8	−4	46·5	32·9	−2·865
8	−3	93·8	83·4	−2·920
8	−2	138·9	130·9	0·199
8	0	104·6	115·0	−2·917
8	1	122·5	129·4	0·192
8	2	87·9	99·4	0·162
8	3	104·0	105·5	−2·883
8	4	39·1	33·4	0·339
8	5	59·8	63·8	0·260
8	6	69·9	71·6	−2·824
10	−11	80·8	68·3	−2·804
10	−8	85·2	86·1	−2·857
10	−6	71·2	72·7	0·296
10	−3	60·2	73·4	0·300
10	0	53·2	59·7	0·354
10	2	58·6	58·7	−2·810
10	5	88·1	83·1	−2·847
12	−9	70·4	67·1	−2·798
12	−8	63·2	55·4	0·261
12	−7	83·5	80·8	0·232
12	−6	93·6	97·9	−2·877
12	−4	131·2	130·6	0·207
12	−3	91·8	103·3	−2·914
12	−1	73·0	70·4	0·322
12	0	74·3	77·9	−2·910
14	−4	105·8	110·9	−2·894
14	−2	92·4	81·0	0·262
14	−1	109·6	107·5	−2·895
14	0	46·1	36·0	−2·990
14	1	73·8	88·4	0·282
14	4	73·3	66·3	0·341

where X, (Y), and Z are the coordinates in Å referred to axes parallel to **a**, (**b**), and **c***. As may be seen from Fig. 3, the equatorial planes of successive bipyramids along the chain are necessarily parallel and very nearly coincident. The substantial difference from ideal D_{5h} geometry lies in the irregularity of the equatorial pentagon, as shown by the angles (in Table 3) scattered widely about the ideal value of 72°. Of course the difference in size between the oxygen and bromine atoms would be expected to lead to unequal angles; it may be considered, however, that the three oxygens and two bromines in the equatorial coordination zone of the protactinium are equivalent in their spatial requirements to the five chlorines in $PaCl_5$.

The double chain structure is an unusual one and it is all the more surprising to find it also in the non-stoichiometric oxide material $Cs_xUO_3Cl_x$ ($x\sim0{\cdot}9$). The disorder resultant on the non-stoichiometry of this compound was not determined by Allpress & Wadsley (1964), but, as all the chlorines are bridging, their shortfall must result either in a reduction of the multiple bridging of the chains or in chain terminations. In the present compound, termination of the chains at irregular intervals could well account for the difficulties we experienced with the upper level data; we have observed no evidence for non-stoichiometry but, as suggested by Allpress and Wadsley, occasional termination of the chains need not introduce any. Irregularities of this sort could well account also for the difficulty of growing sizable crystals and for the poor quality of the few crystals which have been observed.

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The Crystal Structures of 2,2,6,6-Tetramethyl-4-oxopiperidine Derivatives

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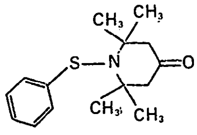
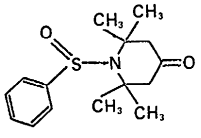
The crystal structures of a series of compounds, 1-benzenesulphenyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPS), 1-benzenesulphinyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO) and 1-benzenesulphonyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO2), have been determined by the three-dimensional Patterson method. The crystals of all three compounds are monoclinic, space group $P2_1/c$, with four molecules in each unit cell of dimensions: $a=17{\cdot}46$, $b=7{\cdot}86$, $c=15{\cdot}51$ Å and $\beta=136{\cdot}0°$ for TMPS, $a=14{\cdot}89$, $b=6{\cdot}31$, $c=21{\cdot}01$ Å and $\beta=130{\cdot}8°$ for TMPSO and $a=7{\cdot}60$, $b=15{\cdot}73$, $c=17{\cdot}08$ Å and $\beta=131{\cdot}2°$ for TMPSO2. Refinements were carried out by the block-diagonal least-squares procedure, and the respective final R values were 0·113, 0·120 and 0·113 for the three molecules. The conformations of the piperidine rings in each compound observed here are a chair form, a twisted form and a boat form. The nitrogen atom in TMPS is sp^3 hybridized, whereas those in TMPSO and TMPSO2 are partly sp^2 hybridized.

Introduction

To study the stereochemistry and the variation of molecular conformation, some tetramethyl piperidine derivatives, (I) 1-benzenesulphenyl-2,2,6,6-tetramethyl-4-oxopiperidine (hereafter designated as TMPS), (II) 1-benzenesulphinyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO) and (III) 1-benzenesulphonyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO2), have been examined by X-ray analysis.



(I)



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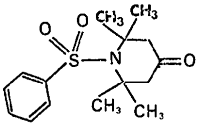

(III)

Analogous compounds with four methyl substituents have been reported by several authors: (IV) S-(2,2,6,6-