Crystal Structure of Bis(tetraethylammonium) oxopentachloroprotactinate(V)

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A three-dimensional structure analysis of the title compound has shown it to be the first example of a protactinium(V) compound to contain a protactinium–oxygen double bond (Pa=O 1·74 Å). Crystals are monoclinic, space-group *Cc*, with $Z = 4$ in a unit cell of dimensions: $a_0 = 14{\cdot}131 \pm 0{\cdot}008$, $b_0 = 14{\cdot}218 \pm 0{\cdot}008$, $c_0 = 13{\cdot}235 \pm 0{\cdot}009$ Å, and $\beta = 91{\cdot}04° \pm 0{\cdot}03°$. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares techniques to *R* 6·7% for 558 independent reflections. The oxygen and five chlorine atoms form a distorted octahedron around the protactinium atom; Pa–Cl distances range from 2·42 to 2·72 Å.

BIS(TETRAETHYLAMMONIUM) oxopentachloroprotactinate(V), $[NEt_4]_2[PaOCl_5]$, is one of four recently prepared protactinium(V) compounds believed to contain a protactinium–oxygen double bond. Thus, although ν(Pa–O) for the solid occurs at an unexpectedly low frequency (830 cm^{-1}), a combination of solution i.r. [ν(Pa–O) 829 cm^{-1}] and conductivity studies have indicated the presence of the $PaOCl_5^{2-}$ ion in the solid rather than the presence of the dimeric ion $Pa_2O_2Cl_{10}^{4-}$ with bridging oxygen atoms.[1] Although several other protactinium(V) mono-oxo-compounds are known, *e.g.* $H_3PaO(SO_4)_3$,[2] $H_3PaO(SeO_4)_3$,[2] $PaO(NO_3)_3,xH_2O$ $(1 < x < 4)$,[3] $PaO(OH)PO_4,H_2O$,[4] and various five-valent oxyhalides,[5-7] structural information is available only for $PaOBr_3$[8] in which chains of protactinium atoms are linked by bridging bromine atoms and cross-linked by three-co-ordinate oxygen atoms. In addition, i.r. data for the remaining compounds either indicate similar polymeric structures (the oxyhalides) or their interpretation is hindered by the presence of other vibrations between 800 and 1000 cm^{-1} (sulphate and selenate). Thus, before the present investigation the existence of a Pa=O had never been conclusively demonstrated.

In view of the unexpectedly low position (829—840 cm^{-1}) of the protactinium–oxygen stretching vibration in compounds of the types $[NEt_4]_2[PaOX_5]$ and $PaOX_3,2Ph_3PO$ ($X = Cl$ and Br) compared with the positions of the metal–oxygen stretching vibrations recorded for $Cs_2[NpOCl_5]$[9] (921 cm^{-1}) and for numerous 3*d* and 4*d* transition-element mono-oxopentahalogeno-complexes[10,11] (922—989 cm^{-1}) it appeared worthwhile to determine the structure of $[NEt_4]_2[PaOCl_5]$ in order to ascertain conclusively whether or not the band at 830 cm^{-1} was associated with a Pa=O.

This is obviously important for i.r. assignments in other protactinium(V) oxo-compounds particularly since ν(M–O) for five-valent *trans*-dioxo-complexes of both 5*f* and 4*d* transition-elements occurs[9-12] in the range 780—832 cm^{-1} and ν(M–O) for certain five-valent compounds containing bridging oxygen atoms occurs between 700 and 885 cm^{-1}.[9-11] In addition, it was of interest to determine the Pa–Cl bond length since ν(Pa–Cl) was assigned to a strong band at 251 cm^{-1} (shoulder at 289 cm^{-1}), a position usually associated with four-valent actinide hexachloro-complexes[12] (255—267 cm^{-1}) and very much lower than the positions recorded for five-valent actinide hexachloro-complexes[12,13] (305—310 cm^{-1}).

EXPERIMENTAL

The compound was prepared as described previously.[1]

Crystal Data.—$C_{16}H_{40}Cl_5N_2OPa$, $M = 684$, Monoclinic, $a_0 = 14{\cdot}131 \pm 0{\cdot}008$, $b_0 = 14{\cdot}218 \pm 0{\cdot}008$, $c_0 = 13{\cdot}235 \pm 0{\cdot}009$ Å, $\beta = 91{\cdot}04 \pm 0{\cdot}03°$, $U = 2670{\cdot}7$ Å^3, $Z = 4$, $D_c = 1{\cdot}704$, $F(000) = 1336$. Space-group *Cc* or *C*2/*c* from systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$), shown to be *Cc* from the successful refinement. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 73{\cdot}4$ cm^{-1}.

Three-dimensional intensity data were collected by use of a virtually spherical crystal of radius 0·1 mm, sealed in a silica capillary to afford protection from the atmosphere and to contain the α-activity, by the multi-film equi-inclination Weissenberg technique. The reciprocal lattice nets $hk0$—8 were surveyed using the same exposure conditions for each layer and the intensities of 558 unique reflections were estimated visually by comparison with a standard scale. Lorentz and polarisation corrections were applied to the estimated intensities following which spherical absorption corrections were applied. The mass absorption coefficient of protactinium was taken to be 118 cm^2 g^{-1} by a linear interpolation from the values published for thorium and uranium.[14]

Structure Determination.—The position of the protactinium atom was derived from a three-dimensional Patterson synthesis. The positions of the oxygen atom and the five

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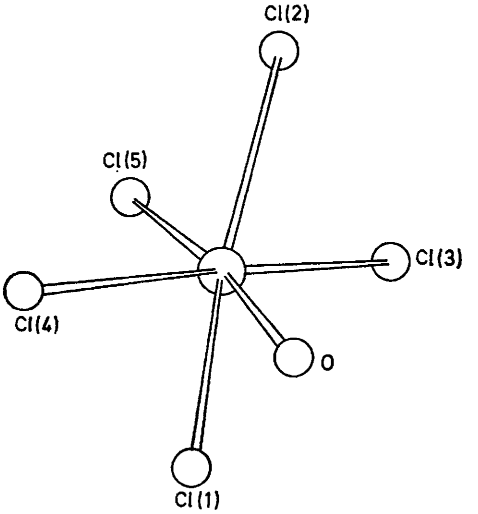
chlorine atoms were obtained from an electron-density synthesis based on protactinium phasing but it was not possible to assign co-ordinates to all the remaining light atoms at this stage. Light-atom co-ordinates (apart from those of the hydrogen atoms) were finally obtained from a difference synthesis based on the protactinium, oxygen, and chlorine positions. Programs NRC 10 (structure-factor and block-diagonal least-squares) and NRC 8 (Fourier summation) were used for these calculations.[15]

TABLE 1

($\Delta f' = -7{\cdot}79$ electrons) of the anomalous dispersion correction was applied since the full-matrix least-squares program available to us [16] has no facility for the introduction of the imaginary part, $\Delta f''$. Scattering factors for the remaining elements were taken from ref. 19. During the initial stages of refinement, individual isotropic thermal parameters were employed and after each cycle individual layer scale-factors were calculated such that $|kF_o| = |F_c|$ for each layer. Individual layer scales varied from 0·3 to 0·5. At this stage the refinement converged to R 8·1% (for and angles were calculated by use of program NRC 12 [20] (scan of interatomic distances and angles) and are listed in Table 2 together with their estimated standard deviations.

DISCUSSION

The oxygen and five chlorine atoms are arranged as a distorted octahedron around the protactinium atom (Figure). The low accuracy of the light atom–light atom distances is probably due to a combination of the relatively small number of observed reflections and the difficulty of accurately locating light atoms in structures containing heavy actinide elements.



The distorted octahedral arrangement around the Pa atom in $(NEt_4)_2$ $PaOCl_5$

The protactinium–oxygen bond length, 1·74 Å, is very similar to M=O bond distances reported for various five-valent 3*d* and 4*d* transition-element mono-oxohalogeno-complexes: $K_2[NbOF_5]$ 1·68,[21] $K_2[MoOF_5],H_2O$ 1·68,[22] $Ph_4As[MoOBr_4],H_2O$ 1·78,[23] and $Ph_4As[ReOBr_4]$,-MeCN 1·73 Å.[24] No metal–oxygen bond distances are available for other five-valent actinide mono-oxo-complexes but the observed bond length lies within the range found for six- and five-valent dioxohalogeno-complexes: $K_3[UO_2F_5]$ 1·76,[25] $[NH_4]_3[UO_2F_5]$ 1·90,[26] $Cs_2[UO_2Cl_4]$ 1·81,[27] $Cs_2[UO_2Br_4]$ 1·69,[28] and $K[AmO_2F_2]$ 1·93 Å.[29]

Although we have established the presence of a protactinium–oxygen double bond in this compound a detailed discussion of the significance of the position of the Pa=O i.r. vibration (830 cm^{-1}) is not warranted in view of the estimated standard deviation associated with this bond length (Table 2). Qualitatively, however, it appears that the accepted diagnostic region [12] (1020—920 cm^{-1}) for ν(M=O) in six-co-ordinate, five-valent *d* transition-element mono-oxo-complexes of types such as $M_2^I[M^VOX_5]$, $M^I[M^VOX_4]$, and $M^VOX_3,2L$ (M^I = univalent cation, M^V = *d* transition element, X = halogen), must be extended for *f* transition-element complexes, at least for those of protactinium(v), to *ca.* 830 cm^{-1}.

The strong protactinium–chlorine stretching vibration at 251 cm^{-1} in the spectrum of $[NEt_4]_2[PaOCl_5]$[1] is probably associated with the longer Pa–Cl bond lengths 2·59—2·72 Å (Table 2) whilst the shoulder at 289 cm^{-1} is associated with the Pa–Cl bond length of 2·42 Å. This short bond [Cl(5) in Figure] is *trans* to the Pa=O bond whereas one might have expected a *trans*-Pa–Cl bond to be longer than the remaining Pa–Cl distances. However, comparison with the only other structural data available for actinide(v) chlorides or chloro-complexes shows that this distance, 2·42 Å, is very much closer to a metal–terminal chlorine bond length than those of the remaining chlorine atoms, 2·59—2·72 Å. Thus for UCl_5,[30] which is a dimeric unit with a distorted octahedron of chlorines around each uranium atom, U–Cl (terminal) is 2·44 Å with U–Cl(bridge) distances 2·67 and 2·70 Å, whilst for $PaCl_5$,[31] which has infinite chains of non-regular pentagonal-bipyramidal $PaCl_7$ groups sharing pentagon edges, Pa–Cl(terminal) distances range from 2·43 to 2·46 Å and the bridging distances from 2·70 to 2·76 Å. The longer Pa–Cl(terminal) distances in $[NEt_4]_2[PaOCl_5]$ are, in fact, very much closer to the metal–chlorine distances reported for the octahedrally co-ordinated four-valent complexes $Cs_2[ThCl_6]$ 2·81,[32] $Cs_2[UCl_6]$ 2·75,[23] and Cs_2PuCl_6 2·62 Å.[33] ν(M–Cl) lies in the range 255—267 cm^{-1} for such complexes [13] (*cf.* the strong band at 251 cm^{-1} for $[NEt_4]_2[PaOCl_5]$).

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