Title

TERTIARY PHOSPHINE DERIVATIVES OF THE f-BLOCK METALS: PREPARATION OF X4M(Me2PCH2CH2PMe2)2, WHERE X IS HALIDE, METHYL AND PHENOXO AND M IS THORIUM OR URANIUM. CRYSTAL STRUCTURE OF TETRA(PHENOXO) BIS-[BIS (1,2-DIMETHYLPHOSPHINO)ETHANE] URANIUM (IV)

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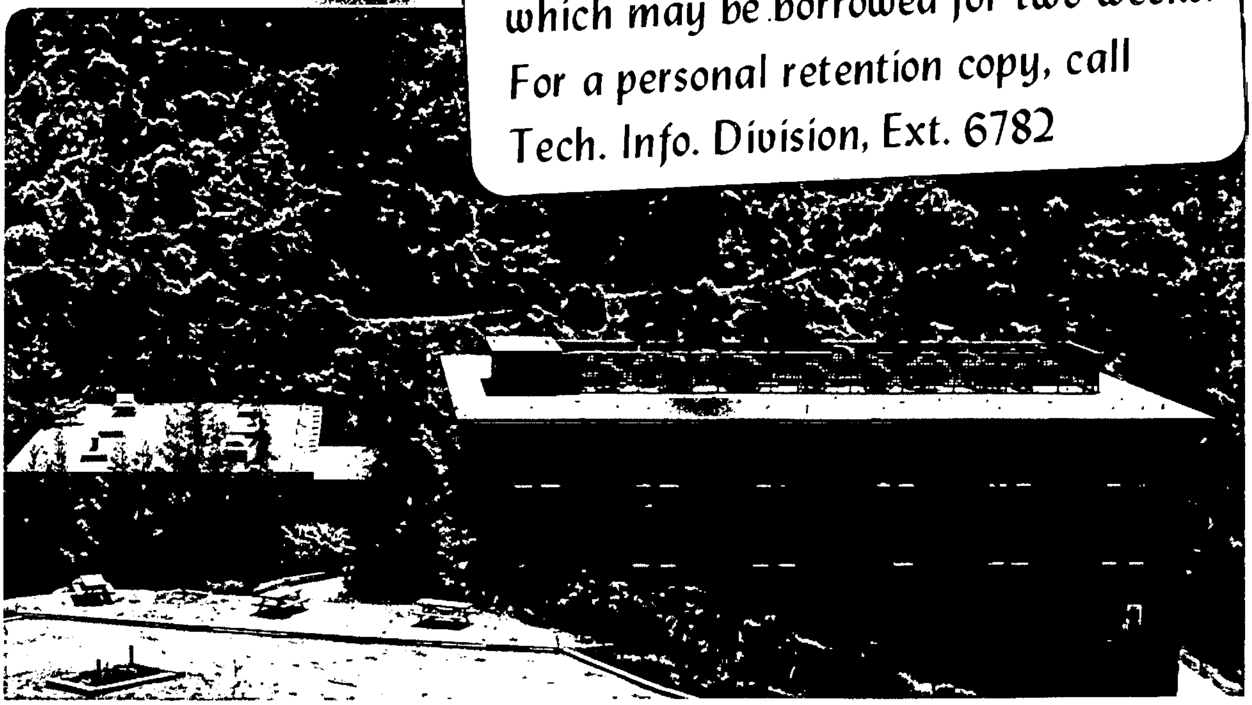
July 1981



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LBL-13065

Tertiary Phosphine Derivatives of the f-Block Metals; Preparation of $X_4M(Me_2PCH_2CH_2PMe_2)_2$, where X is Halide, Methyl and Phenoxo and M is Thorium or Uranium. Crystal Structure of Tetra(Phenoxo)Bis[bis(1,2-dimethylphosphino)-ethane] uranium(IV)

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ABSTRACT

Authentic phospine complexes of the actinide metals (thorium and uranium) of the type $X_4M(Me_2PCH_2CH_2PMe_2)_2$, where X is Cℓ, Br, PhO, or Me and M is U and where X is Cℓ, I, PhO, or Me and M is Th, have been prepared. The crystal structure of the uranium-phenoxide, $(PhO)_4U(dmpe)_2$, is described.

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Though a number of tertiary phosphine complexes of uranium halides have been claimed,[1] most of the claims have been shown to be false.[2] In this communication we describe the synthesis of some authentic bis(1,2-dimethylphosphino)ethane, dmpe, complexes of uranium(IV) and thorium(IV) halides of the type $X_4M(dmpe)_2$ and their conversion to the tetramethyl and tetraphenoxo derivatives. The crystal structure of the phenoxo derivative, $(PhO)_4U(dmpe)_2$, is described.

Uranium tetrachloride dissolves in a mixture of dichloromethane and a three-fold molar excess of bis(1,2-dimethylphosphino)ethane, dmpe, at room temperature to give a blue green solution from which green prisms of $UC\ell_4(dmpe)_2$ may be crystallized on cooling (-20°C).[3,4] The complex is a non-conductor in $CH_2C\ell_2$ and gives only free dmpe upon hydrolysis with water as judged by $^{31}P\{^1H\}$ NMR spectroscopy. The complex may be quantitatively recrystallized from either diethyl ether or tetrahydrofuran. Thus, in a qualitative sense, the Lewis acidity of the uranium atom in $UC\ell_4$ lies in the order: dmpe>thf, Et_2O. Further, the complex may be sublimed at 160°C at 10^{-3} mm. with only partial decomposition to $UC\ell_4$ and a molecular ion is observed in the mass spectrum. Thus the phosphine complex is rather robust, suggesting the uranium-phosphine interaction is not thermodynamically weak.

The uranium tetrabromide and thorium tetraiodide complexes, $MX_4(dmpe)_2$ where M is U and X is Br[5] or M is Th and X is I[6], may be prepared similarly. The iodide complex is a non-conductor

($CH_2C\ell_2$) and only gives free dmpe upon hydrolysis with water as shown by $^{31}P\{^1H\}$ NMR spectroscopy. In contrast, thorium tetrachloride does not dissolve in a solution of dmpe in dichloromethane. However, $ThC\ell_4$ dissolves in neat phosphine at 80°C to give a colorless solution from which $ThC\ell_4(dmpe)_2$ may be obtained. The complex is crystallized from dichloromethane as colorless prisms (-20°C),[8] and is a non-conductor ($CH_2C\ell_2$).

The chloro-phosphines of uranium or thorium react with four molar equivalents of methyllithium in diethyl ether at 0°C to yield the tetramethyl derivatives $Me_4U(dmpe)_2$[9] as brown-yellow prisms from pentane (-70°C) or $Me_4Th(dmpe)_2$[10] as colorless prisms from pentane (-70°C), respectively. Though $Me_4M(dmpe)_2$, where M is Th or U, must be prepared at 0°C, they are sufficiently thermally stable at 25°C to afford satisfactory elemental analysis. They appear to be indefinitely stable below -20°C in absence of air and moisture. The relative thermal stability of the phosphine complexes is noteworthy, since the tetravalent, anionic, methyl derivatives, e.g., $[Li_2(OEt_2)_8]Me_6U$, decompose at approximately -20°C.[11] Both dmpe complexes react with hydrogen chloride in toluene to give $C\ell_4M(dmpe)_2$, where M is Th or U, and methane.

The alkyl-phosphine complexes react with phenol in toluene to give green $(PhO)_4U(dmpe)_2$ and colorless $(PhO)_4Th(dmpe)_2$. The phenoxides react with four molar equivalents of methyllithium to give the tetraalkyls, $Me_4M(dmpe)_2$ where M is Th or U. Both phenoxides crystallize from toluene as toluene solvates $(PhO)_4M(dmpe)_2.C_7H_8$ (M=U,[12] M=Th[13]).

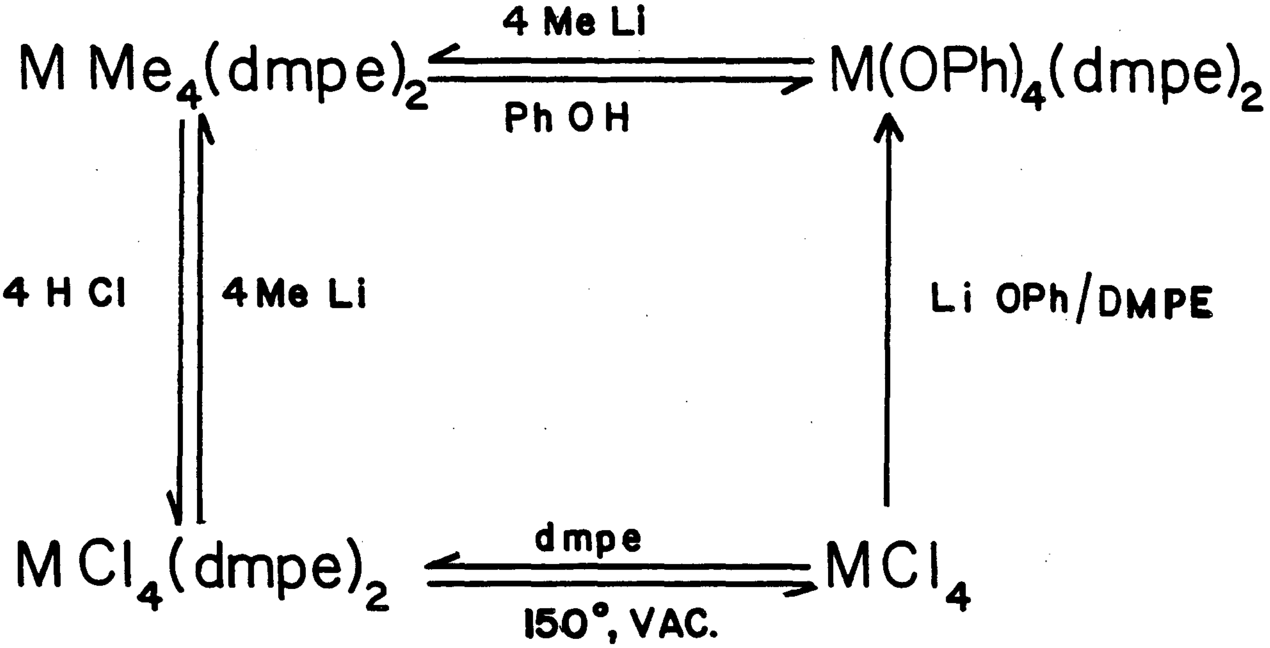
Since the uranium complexes may be converted into each other (Scheme), the crystal structure of any one of them proves the existence of all of them as authentic tertiary phosphine complexes of uranium. In addition, the infrared spectrum and powder X-ray diffraction pattern of $U(OPh)_4(dmpe)_2$ are identical with those of $Th(OPh)_4(dmpe)_2$. Thus, the thorium phenoxide is isostructural with its uranium analogue. Since the thorium derivatives may be converted into each other, they are also authentic phosphine complexes.

An ORTEP[14] diagram of $U(OPh)_4(dmpe)_2$ is shown in Figure I and a line drawing is shown in Figure II with some bond angles and lengths. The coordination polyhedron is related to that of a D_{2d} dodecahedron with the four phosphorus atoms and the four oxygen atoms occupying the A and B sites, respectively.[15] The shape parameters will be discussed in a full paper. The average uranium-oxygen bond length of 2.17 ± 0.01Å is in the range observed for other uranium alkoxide-oxygen bonds.[16] The average uranium-phosphorus bond length of 3.104 ± 0.006Å is unique so no direct comparison is possible, though an estimate can be made. The tetrahedral covalent radius of a phosphorus atom is 0.44Å larger than that of an oxygen atom.[17] Hence a uranium-phosphorus bond length of 2.6Å may be estimated, rather shorter than that observed. On the other hand, a value of 2.9-3.0Å may be estimated from the eight coordinate $MX_4(diars)_2$ complexes, where M is a group IVb or Vb metal, when the radii of arsenic and the transition metals are taken into account.[18] The latter estimated value is much closer to the value observed.

Acknowledgement

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

Supplementary Material Available: Positional and thermal parameters and estimated standard deviations and estimated atomic parameters for the hydrogen atoms and anisotroic thermal parameters (3 pages) are available. Ordering information is given on any current masthead page.



4 Me Li
M Me$_4$(dmpe)$_2$
M(OPh)$_4$(dmpe)$_2$
Ph OH
4 H Cl
4 Me Li
Li OPh/DMPE
dmpe
M Cl$_4$(dmpe)$_2$
M Cl$_4$
150°, VAC.

Scheme

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3 *Anal*. Calcd. for $C_{12}H_{32}C\ell_4P_4U$:C,21.2; H,4.71; Cℓ,20.9. Found: C, 21.6; H, 4.77; Cℓ, 22.0; M^+(680). NMR: $^1H(PhMe\text{-}d_8$, 26°C), $\delta 2.09s(\nu_{1/2}=4.1$ Hz). $^{13}C\{^1H\}(PhMe\text{-}d_8$, -60°C): $\delta{-2.04}s(\nu_{1/2}=14.7$ Hz) and $\delta{-6.84}s(\nu_{1/2}=17.6$ Hz). No resonance was observed in $^{31}P\{^1H\}$ NMR experiments, not even a resonance due to free dmpe.

4. The trimethylphosphine derivative, $UC\ell_4(PMe_3)_3$ was prepared similarly. <u>Anal</u>. Calcd. for $C_9H_{27}C\ {}_4P_4U$: C, 17.8; H, 4.44; C , 23.3 found: C, 17.0; H, 4.63; Cℓ, 22.7. The sample must be crystallized from neat PMe_3, otherwise analyses were not reproducible due to ready loss of phosphine.

5 Green prisms were obtained from $CH_2C\ell_2$. <u>Anal</u>. Calcd. for $C_{12}H_{32}Br_4P_4U$: C, 16.8; H, 3.73; Br, 37.3. Found: C, 16.9, H, 3.81; Br, 37.0. NMR; $^1H(PhMe\text{-}d_8$, 26°C), $\delta 3.38s(\nu_{1/2}=3.1$ Hz).

6. Colorless prisms were obtained from $CH_2C\ell_2$. <u>Anal</u>. Calcd. for $C_{12}H_{32}I_4P_4Th$: C, 13.9; H, 3.08; I, 48.8. Found: C, 14.0; H, 3.22; I, 47.4. NMR: $^1H(CD_2C\ell_2$, 26°C), the methylene protons appear as a filled-in doublet centered at $\delta 2.11$ with a separation between the outer lines of 14 Hz and the methyl protons appear as a five line pattern centered at $\delta 1.76$ with a separation between the outermost lines of 7.6 Hz.[7]

$^{31}P\{^1H\}$ ($CD_2C\ell_2$, 25°C), δ-17.8. The coordination chemical shift, defined as the chemical shift of the complex less that of the free ligand, is 31.6 ppm.

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8. Anal. Calcd. for $C_{12}H_{32}C\ell_4P_4Th$: C, 23.5; H, 5.23; Cℓ, 23.7. Found: C, 23.5; H, 5.16; Cℓ, 22.9. NMR: ^1H(PhMe-d_8, 24°C), the methylene protons are an apparent singlet at $\delta 2.31(\nu_{1/2}=4.5$ Hz).[7] The methyl protons are an apparent singlet at $\delta 1.46$, $(\nu_{1/2}=8$ Hz). $^{13}C\{^1H\}$(PhMe-d_8, -60°C), the methylene carbon atoms appear as a seven-line pattern centered at $\delta 25.9$ with the separation of the outermost lines being 26.6 Hz. The methyl carbon atoms are an apparent singlet at $\delta 11.6$, $(\nu_{1/2}=2$ Hz).[7] $^{31}P\{^1H\}$ (PhMe-d_8, 26°C), a singlet at δ-9.85. The coordinate chemical shift is 39.5 ppm.

9. Anal. Calcd. for $C_{16}H_{44}P_4U$: C, 32.1; H, 7.36. Found: C, 31.7; H, 7.29. NMR: ^1H(PhMe-d_8, -70°C). Three apparent singlets, $(\nu_{1/2}=40.5$, 12.1 and 32.4 Hz), are observed at δ-42.4, -1.76, and 10.1 respectively in area ratio 8:24:12 due to $Me_2P\underline{CH_2}$, $\underline{Me_2}PCH_2$, and $\underline{Me_4}U$, respectively. The ^{13}C(PhMe-d_8, -40°C) yields an apparent quartet centered at δ-38.8 ($J_{CH}=137$ Hz) and an apparent triplet centered at δ-63.2 ($J_{CH}=137$ Hz) due to the methyl and methylene groups of coordinated dmpe. No resonance was observed for the Me-U carbon atom.

10. Anal. Calcd. for $C_{16}H_{44}P_4Th$: C, 32.4; H, 7.43; P, 20.9. Found: C, 32.7; H, 7.30; P, 20.4. NMR: ^1H(PhMe-d_8, -50°C). The Me-Th resonance appears as a binomial pentet centered at δ-0.09 ($J_{PH}=2.87$ Hz) and the Me-P and CH_2-P resonances appear as an apparent singlet at $\delta 1.33(\nu_{1/2}=2$ Hz) and an apparent

doublet centered at δ1.45, the separation between the outer lines in the latter resonance is 23 Hz. ^{13}C(PhMe-d_8, -80°C), a quartet centered at δ10.5 (J_{CH}-128 Hz), a triplet centered at δ28.0 (J_{CH}=134 Hz) and a quartet centered at δ46.3 (J_{CH}=107 Hz) due to $\underline{Me_2}$P, $\underline{CH_2}$P, and $\underline{Me_4}$Th, respectively. The $\nu_{1/2}$ of each resonance is ca. 4 Hz. ^{31}P{^{1}H} (PhMe-d_8, -80°C), a singlet at δ-27.6.

11. Sigurdson, E.R.; Wilkinson, G. J. Chem. Soc. Dalton Trans., 1977, 812-818.

12 Anal. Calcd. for $C_{43}H_{60}O_4P_4U$: C, 51.5; H, 5.99. Found: C, 51.3; H, 5.98. NMR: ^{1}H(PhMe-d_8, -24°C). Three resonances are attributable to the phenyl protons at δ33.45, doublet (J_{CH}=7.3 Hz); δ15.59, binomial triplet (J_{CH}=7.3 Hz) and δ13.59, binomial triplet (J_{CH}=7.3 Hz) in area ratio 8:8:4 due to meta, ortho and para protons, respectively. The resonances due to dmpe occur as broad, apparent singlets at δ-3.78 ($\underline{Me_2}$P) and δ-32.86 ($\underline{CH_2}$P), ($\nu_{1/2}$=40 Hz in each case) in area ratio 24:8, respectively. Resonances due to toluene of crystallization appear at δ7.04, singlet and δ2.12, singlet, due to the phenyl and methyl protons in area ratio 5:3, respectively.

13. Anal. Calcd. for $C_{43}H_{60}O_4P_4Th$: C, 51.8; H, 6.02. Found: C, 52.1; H, 5.98. NMR: ^{1}H(PhMe-d_8, 40°C). The phenyl resonance appears as a broad ($\nu_{1/2}$=41 Hz) complex multiplet centered at δ7.04 and includes the phenyl resonance of toluene of crystallization. The methyl protons of toluene give rise to a singlet (δ2.14), dmpe protons an apparent three line pattern with

the central line at δ1.16 and the separation between the two outer lines being 12.2 Hz and a broad singlet, δ0.82 ($\nu_{1/2}$=6 Hz, $\underline{Me}_2P$). The resonances have relative area ratios 25:3:8:24. $^{13}C\{^1H\}$ ($CD_2C\ell_2$, -50°C). The aromatic carbons give rise to four singlets at δ167.44 (α to oxygen), 128.91 (β to oxygen), 119.50 (γ to oxygen) and 115.99 (δ to oxygen). Assignment is confirmed by the ^{13}C spectrum where the three high field signals are observed as doublets (J_{C-H}=148.4, 159.2 and 161.1 Hz, respectively) and the quaternary carbon (δ167.44) remains as a singlet. Dmpe gives rise to two broad singlets at δ27.06 ($P-\underline{CH}_2$, $\nu_{1/2}$=32 Hz) and δ13.23 ($\underline{Me}_2P$, $\nu_{1/2}$=35 Hz). $^{31}P\{^1H\}$ (PhMe-d_8, 100°C). δ-35.30, broad singlet ($\nu_{1/2}$=43 Hz) The coordination chemical shift is 14.0 ppm.

14. The crystals are triclinic, $P\bar{1}$, with cell dimensions $\underline{a}$ = 12.560(4)Å, $\underline{b}$ = 12.831(4)Å, $\underline{c}$ = 15.012(4)Å, α = 77.84(3)Å, β = 83.28(3)Å, and γ = 88.94(3)Å. For two molecules in the unit cell the calculated density is 1.29 g/cm^3. Intensity data were collected with a Nonius CAD-4 automated X-ray diffractometer using Mo Kα X-rays. The structure was solved by the "heavy-atom" technique and refined by full-matrix least-squares to an R factor of 0.052 using 5090 reflections in which $F^2 > 3\sigma(F^2)$.

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Figure Captions

Figure 1. A view of the $U(OPh)_4(dmpe)_2$ molecule showing the phenoxy groups in a distorted equatorial environmental.

Figure 2. Schematic representation of the structure of $U(OPh)_4(dmpe)_2$ showing relevant averaged bond angles and bond lengths. Angle A = 94.6 ± 0.4°, Angle B = 147.2 ± 0.1°, Angle C = 64.7 ± 0.6°, Angle D = 135.5 ± 2.2°, U--O = 2.17 ± 0.01Å, U--P = 3.104 ± 0.006Å.

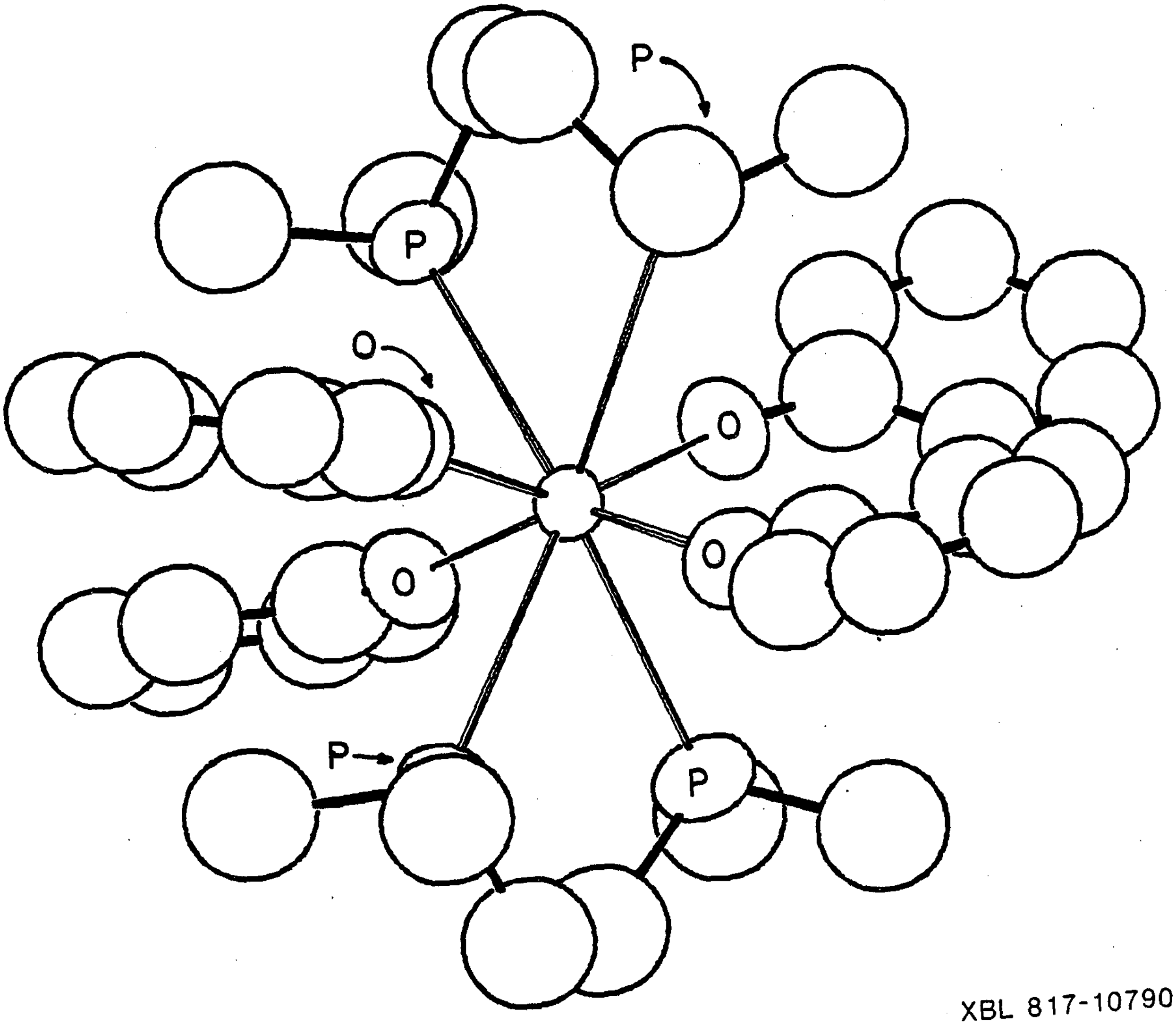
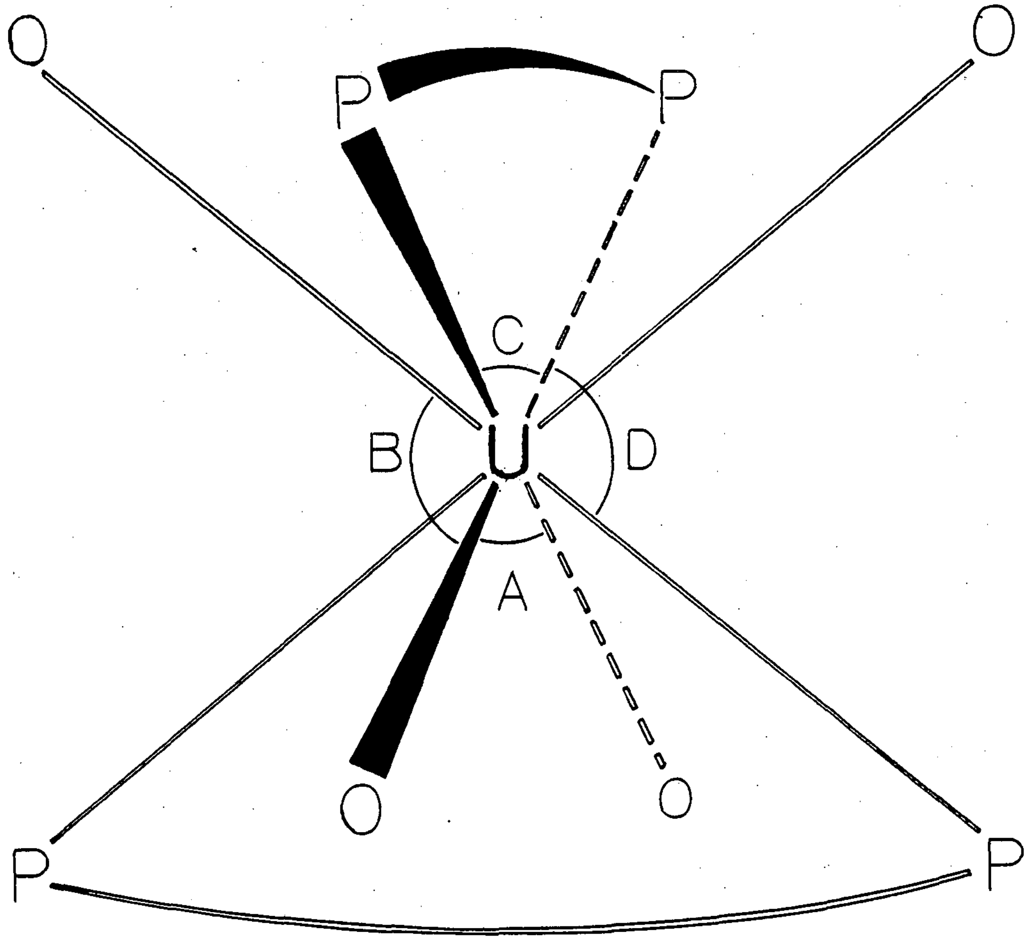


Figure 1



XBL 818-10948

Figure 2

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