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PREPARATION OF $MCl_4(Me_2ECH_2CH_2EMe_2)_2$ AND $MCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$ WHERE M IS THORIUM OR URANIUM AND E IS NITROGEN OR PHOSHORUS. CRYSTAL STRUCTURE OF $UCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$

P.G. Edwards, R.A. Andersen, and R.W. Gellert

July 1986

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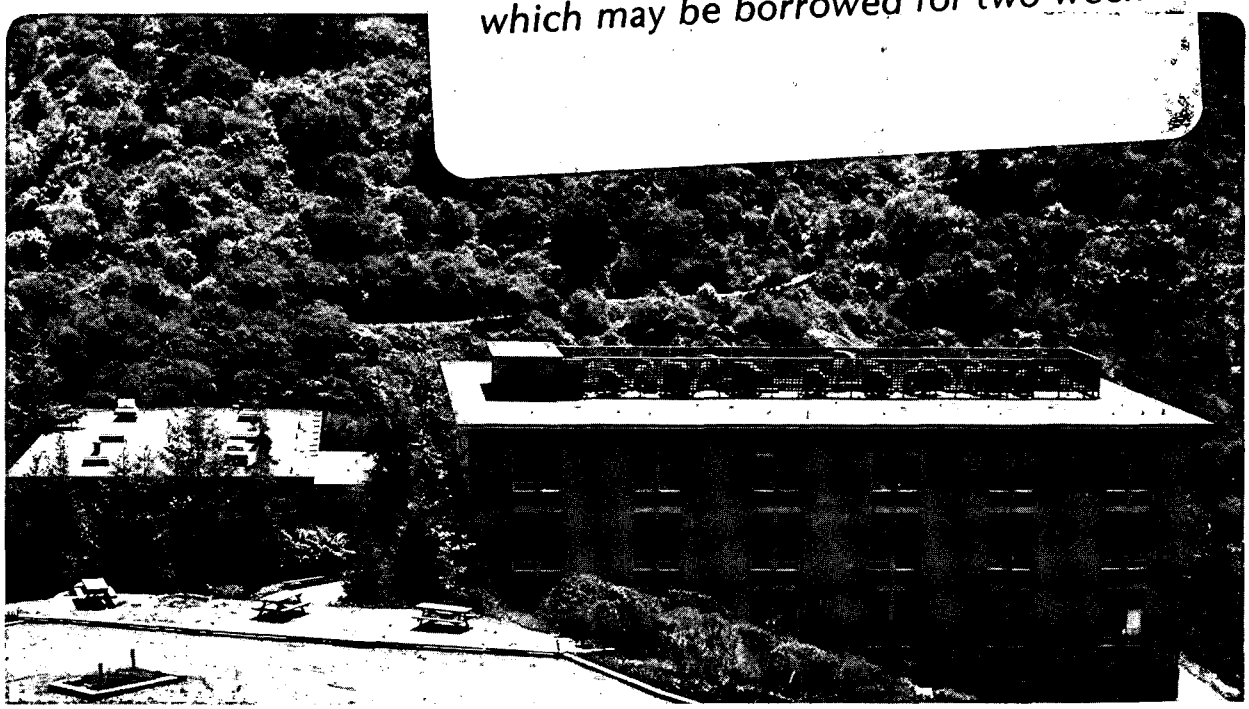

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-21473

Preparation of $MCl_4(Me_2ECH_2CH_2EMe_2)_2$ and $MCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$ where M is Thorium or Uranium and E is Nitrogen or Phosphorus. Crystal Structure of $UCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$.

Peter G. Edwards,[a] Richard A. Andersen,[a*] and Robert W. Gellert[b]

a) Chemistry Department and Materials and Molecular Research Division of Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

b) Chemistry Department, California State University, Los Angeles, Los Angeles, California 90032.

*Address all correspondence to this author at Chemistry Department, University of California, Berkeley.

Abstract

The compounds $MCl_4(Me_2ECH_2CH_2EMe_2)_2$ where M is Th or U and E is N or P have been prepared. Variable temperature NMR spectra show that the geometry of the eight coordinate complexes are based upon that of a D_{2d}-dodecahedron with the chloride ligands on the B-sites and the nitrogen or phosphorus atoms on the A-sites. The nitrogen complexes, $MCl_4(tmed)_2$, are fluxional on the ^1H NMR time scale and the fluxional process is suggested to be the $\Lambda = \Delta$ motion of the ethylene-backbone in the five-membered ring of $MN(Me)_2CH_2CH_2NMe_2$ that is fast at high temperature and slow at low temperature. The complexes $MCl_4(dmpe)_2$ are fluxional at all temperatures. The arsenic complexes $MCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$ have also been prepared for M = Th or U. Crystals of $UCl_4(diars)_2$ are tetragonal, $I\bar{4}2m$ with a = 9.407(1) and b = 17.318(2)A, z = 2, V = 1532.5A^3, d (calc) = 2.063 g cm^{-3}, and d (obsd) is 2.07 g cm^{-3}. The structure was refined by full matrix least-squares to a conventional R-factor of 0.020 using 556 data with $F_o^2 > 2\sigma(F_o^2)$. The geometry is almost a perfect D_{2d}-dodecahedron with the chloride ligands on the B-sites and the arsenic atoms on the A-sites. The U-As distance is 3.049(1)A and the U-Cl distance is 2.618(3)A. Qualitative equilibrium constant studies in toluene show that for UCl_4 the ligand displacement series is dmpe > tmed > diars and for the $ThCl_4$ the series is dmpe ≥ tmed > diars.

Several tertiary phosphine complexes of the f-block metals have been claimed, though most of these claims have been shown to be erroneous.[1a] We have described recently the successful preparation of actinide[1b] and lanthanide[1c,d] complexes with the bidentate phosphine ligand bis-1,2-dimethylphosphinoethane, dmpe. The trivalent and tetravalent uranium complexes, $U(C_5Me_5)_2(H)(dmpe)$[2a] and $U(BH_3Me)_4(dmpe)$[2b] respectively, as well as other phosphine complexes have been reported.[2c-f] The literature on tertiary arsine complexes of the f-block elements is as confusing as that of the tertiary phosphine complexes. It has been claimed that thorium tetrachloride does not yield a complex with bis-1,2-dimethylarsinobenzene, diars.[3a] Further, neither uranium tetrachloride nor the tetrabromide are said to give diars complexes,[3b] though a light yellow, insoluble, 1:1 complex[3c] and a blue-grey, insoluble, 1:2 complex of uranium tetrachloride have been reported.[3d]

As a consequence of the inability to isolate simple actinide coordination complexes of phosphines, the actinide metals have been classified as class a or hard acceptors.[4] This classification, based upon ligand displacement reactions, classifies those acceptors whose coordinative affinity for a given Group 5 donor lies in the order N >> P > As as a class a and those acceptors whose coordinative affinity lies in the order N << P < As as class b. The classification scheme is generally accepted though the reasons for its origin are controversial.[5] The isolation of phosphine complexes of the actinide metals appears to challenge the class a classification of these metals. However, isolation of phosphine complexes, by itself, does not address the

question of classification and a study of ligand displacement reactions is required. In this paper we describe the preparation and crystal structure of $UCl_4(diars)_2$, a preliminary study of ligand displacement equilibria, and full synthetic details for complexes of the type MX_4(bidentate Ligand)$_2$.

Synthetic and Spectroscopic Studies. In order to determine equilibrium constants for the ligand displacement reactions we needed to prepare a series of complexes of the type $MCl_4(Me_2ECH_2CH_2EMe_2)_2$ where M is thorium or uranium and E is nitrogen, phosphorus, or arsenic. The phosphine complexes have been described briefly.[1b] The structure of eight coordinate $U(OPh)_4(Me_2PCH_2CH_2PMe_2)_2$ is based upon a D_{2d}-dodecahedron with the oxygen atoms on the B-sites and the phosphorus atoms on the A-sites. The halide complexes of thorium and uranium are presumed to have a similar structure.[6] Solution spectroscopic properties are consistent with, though do not prove, the solid state structure since the low temperature ^1H and ^{13}C NMR spectra of the complexes show that the methyl and methylene groups are equivalent, see experimental section for details. These results, however, do not rule out rapid fluxional processes that cause the resonances to be equivalent on the NMR time scale since stereochemical nonrigidity is common in eight coordination.[7]

Unfortunately the directly related arsenic ligand, $Me_2AsCH_2CH_2AsMe_2$, can only be prepared with difficulty and in low, erratic yields.[8] Consequently, we chose to prepare complexes with the related diarsenic ligand, bis-1,2-dimethylarsinobenzene, diars.[9] The thorium or uranium tetrachloride complexes, $MCl_4(diars)_2$, may be

prepared by allowing the metal tetrachlorides to dissolve in the neat ligand, followed by crystallization from dichloromethane.

The ^{1}H NMR spectra of both complexes show singlets at δ 1.59 (M=Th) and 1.79 (M=U) for the methyl groups. The aromatic protons comprise an AA'BB' spin system, the A protons being ortho and the B protons being meta to the Me_2As groups. The spectra were simulated in a AA'BB' spin system with $\delta A = \delta A' = 1.02$, $\delta B = \delta B' = -4.01$, $J_{AB} = 8.0$Hz, $J_{BB'} = 7.0$Hz, $J_{A'B} = 1.25$Hz, and $J_{AA'} = 0.5$Hz for the uranium complex and $\delta A = \delta A' = 7.67$, $\delta B = \delta B' = 7.00$, $J_{AB} = 8.0$Hz, $J_{BB'} = 7.0$Hz, $J_{A'B} = 1.25$Hz, and $J_{AA'} = 0.5$Hz for the thorium complex.[10] The $^{13}C\{^1H\}$ NMR spectra, which are listed in the experimental section, also show that the two diarsine ligands in $MCl_4(diars)_2$ are equivalent. This is also true in the solid state as shown below.

The nitrogen analogues of the phosphine complexes are unknown though they may be prepared by reaction of thorium or uranium tetrachloride with $Me_2NCH_2CH_2NMe_2$(tmed) in toluene. The structure of $UCl_4(Me_2NCH_2CH_2NMe_2)_2$ is based upon a D_{2d}-dodecahedron with the chloride ligands occupying the B-sites and the nitrogen atoms occupying the A-sites.[6] Further, $UCl_4(tmed)_2$ and $UCl_4(dmpe)_2$ are isostructural in the solid state and we postulate that all of the compounds described in this manuscript are isostructural. The amine complexes, however, are fluxional molecules in solution. Thus, the ^{1}H NMR spectrum of $ThCl_4(tmed)_2$ at +56°C in toluene-d_8 shows two singlets at δ2.74 (ν 1/2 = 1Hz) and 2.41 (ν 1/2 = 5Hz) in area ratio 3:1. The former resonance is due to the N-Me and the latter is due to the N-CH_2 protons. Lowering the temperature to -40°C results in the splitting of the N-Me protons

into two equal area singlets at δ2.80 and 2.67 (ν 1/2 = 5Hz for each resonance) and the N-CH_2 protons appear as a pair of doublets centered at δ 3.01 and 1.47 with ν 1/2 for each resonance of 13Hz and a doublet separation of 12Hz. Homonuclear decoupling shows that the doublets are related since irradiation of one doublet causes the other doublet to collapse into a singlet. Clearly the methyl and methylene protons are not equivalent and each $Me_2NCH_2CH_2NMe_2$ group may be described by the spin system $X_3X'_3AA'BB'Y_3Y'_3$. The decoupling experiments show that the spectrum is due to a single species in solution. The ^1H NMR spectrum in chloroform-d_1 is qualitatively similar to that in toluene. At +56°C a single resonance is observed at 300MHz at δ2.87 (ν 1/2 = 1Hz) and at -61°C the N-Me resonance appears as a pair of singlets at δ2.85 and 2.84 and the N-CH_2 resonance appears as a pair of doublets centered at δ3.45 and 2.28 with J = 12Hz and ν 1/2 for all the resonances being ca. 6Hz.

The ^{13}C NMR spectrum of $ThCl_4(tmed)_2$ in toluene-d_8 supports the ^1H NMR spectral data. At 27°C two resonances are observed, a triplet centered at δ58.7 (J_{CH} = 134Hz) and a quartet centered at δ50.9 (J_{CH} = 136Hz). Lowering the temperature to -50°C causes the methyl resonance in the $^{13}C\{^1H\}$ NMR spectrum to split into two equal area resonances at δ52.4 and 49.6 though the methylene resonance remains a singlet. Thus the methyl carbon atoms are non-equivalent though the methylene carbon atoms are equivalent.

The NMR spectra of paramagnetic (f^2) $UCl_4(tmed)_2$ are related to those of the diamagnetic thorium analogue, with the exception that all of the coupling information in the paramagnetic molecule is lost. The ^1H NMR spectrum in methylenechloride-d_2 at -80°C shows two equal area

singlets at δ17.6 and -17.0 (ν 1/2 in each case of 10Hz) due to the methyl protons and two singlets at δ -51.4 and -90.0, with ν1/2 of 20Hz each, due to the methylene protons. At 25°C the resonances occur at δ 3.2 and -0.8 (ν 1/2 = 120Hz) and δ -10.9 and -20.3 (ν 1/2 = 90Hz) for the methyl and methylene protons, respectively. The $^{13}C\ \{^1H\}$ NMR spectrum at -50°C in methylenechloride-d_2 shows three resonances at δ 23.1 (ν 1/2 = 20Hz), -1.60 (ν 1/2 20Hz), and -95.6 (ν 1/2 = 55Hz), due to the non-equivalent methyl carbons and the equivalent methylene carbons, respectively.

Qualitatively similar ^1H and $^{13}C\ \{^1H\}$ NMR spectra of the type observed for $MCl_4(tmed)_2$ have been observed previously in $M(CO)_4(tmed)$, where M is chromium, molybdenum, and tungsten.[12] The inequivalence of the methyl protons, methylene protons, and methyl carbons and the equivalence of methylene carbons at low temperature was ascribed to a Λ = Δ barrier to interconversion in the five-membered chelate ring. We invoke a similar explanation for the fluxional processes in the $Me_2NCH_2CH_2NMe_2$ complexes prepared in this work.

A diagram of the molecules $MX_4(Me_2ECH_2CH_2EMe_2)_2$ with idealized D_{2d}-dodecahedral symmetry is shown in Figure I. In this symmetry the methyl and methylene group protons are equivalent and the ^1H NMR spectrum will show two resonances in an area ratio of 24:8. The D_{2d}-symmetry is maintained when the ethylene-backbone of the $Me_2ECH_2CH_2EMe_2$ ligand is fluxional and the interconversion between Λ and Δ isomer is rapid. However, if the Λ = Δ interconversion is slow, then the symmetry planes in D_{2d}-symmetry are removed and the molecule has D_2-symmetry. In idealized D_2-symmetry the methyl and methylene protons

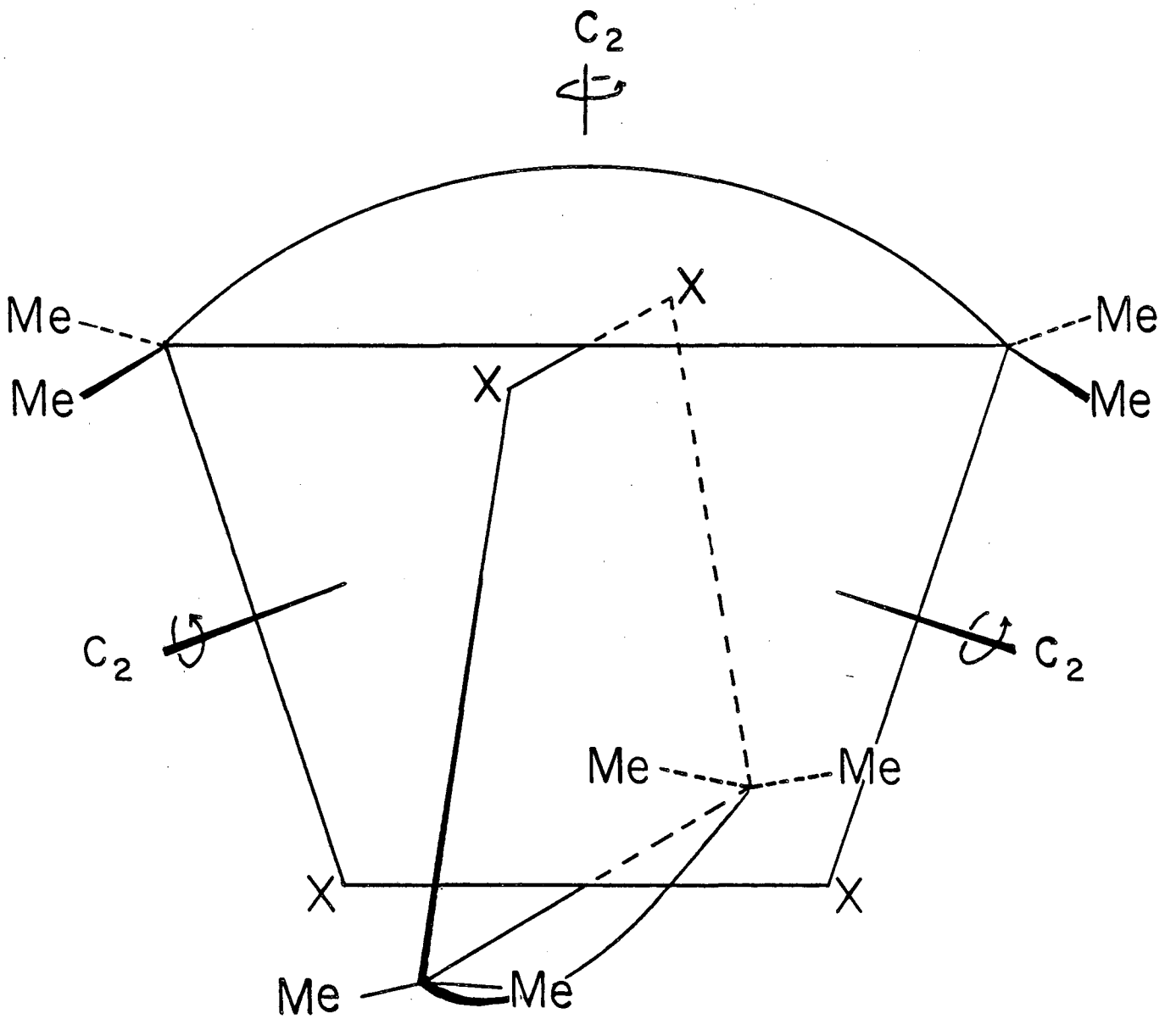

Figure I

are pairwise inequivalent and the spin system for $MCl_4(Me_2ECH_2CH_2EMe_2)_2$ is $[X_3X'_3AA'BB'Y_3Y'_3]_2$. A diagram is shown in Figure II, down the C_2-axis. In the low temperature ^1H NMR spectrum of $MCl_4(tmed)_2$ the methyl region appears as two broadened resonances with $\delta X = \delta X'$ and $\delta Y = \delta Y'$. None of the coupling constants are resolved so a broadened resonance results. The methylene resonances have a similar appearance with $\delta A = \delta A'$ and $\delta B = \delta B'$. In the $^{13}C\ \{^1H\}$ NMR spectrum, the methyl carbons are inequivalent and the methylene carbons are equivalent and the spectra show three equal area resonances. The spectra of $MCl_4(tmed)_2$, M = Th or U, below ca. -60°C show this behavior. At high temperature, ca. +60°C, the spectra of $ThCl_4(tmed)_2$ are similar to those found for all temperatures for the phosphine complexes, i.e., the methyl groups and the methylene groups are equivalent.

We interpret these variable temperature results by assuming that the molecules are undergoing intra-molecular exchange and that the low temperature solution structure is the same as that found in the solid state. The simplest explanation is that the ethylene protons of the $Me_2NCH_2CH_2NMe_2$ ligand are undergoing a $\Lambda = \Delta$ interconversion that is slow at -60°C but fast at +60°C. This postulate requires that the barrier in $MCl_4(dmpe)_2$ is low and the phosphine complexes are fluxional at all temperatures, which suggests that the origin of the barrier is steric. In the crystal structure of $UCl_4(tmed)_2$,[6] the chloride ligands are in a staggered configuration relative to the nitrogen methyl groups as shown diagramatically in Figure II. The long U-N bond distance of 2.79 ± 0.02Å is ca. 0.1Å longer than expected on the basis of the U-P distance in $U(OPh)_4(dmpe)_2$[1] of 3.104 ± 0.006Å since the covalent radius

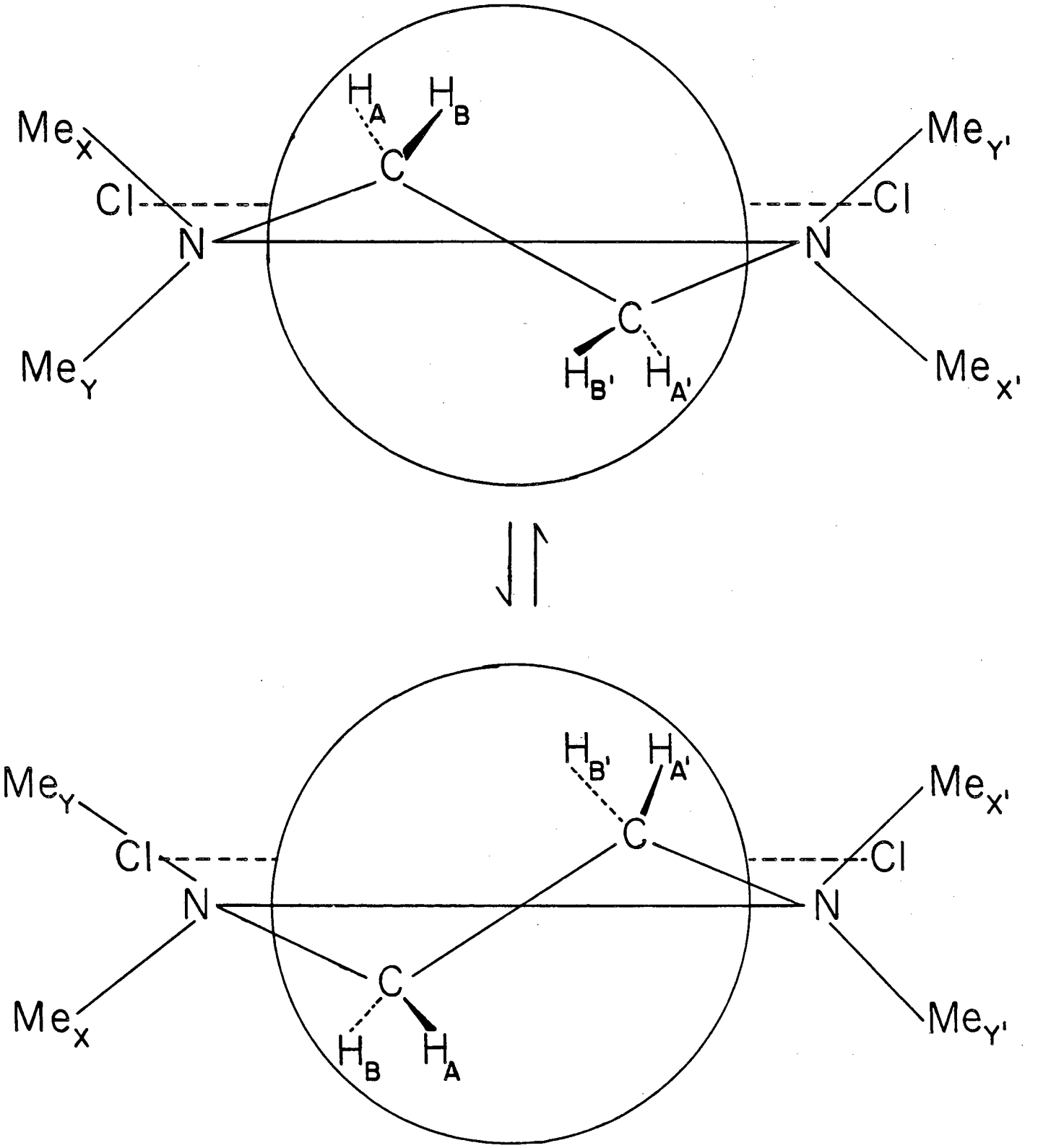
Me X
Cl
N
Me Y
H A
H B
C
C
H B'
H A'
N
Cl
Me Y'
Me X'
Me Y
Cl
N
Me X
H B'
H A'
C
C
H B
H A
N
Cl
Me X'
Me Y'

Figure II

of nitrogen is 0.40Å smaller than phosphorus.[13a] Even though the U-N distance is long, the non-bonded contact distances between the N-methyl carbon atoms and the chloride ligands are ca. 3.4Å, close to the sum of the van der Waals radii for these two atoms.[13b] Interconversion of the Λ and Δ conformers by way of an envelope transition state[14] requires that the N-methyl groups move into an eclipsing configuration with the chloride ligands which increases the non-bonded repulsion energy and therefore the interconversion barrier.

Ligand Displacement Studies. We conducted a series of displacement studies by mixing an excess of free ligand with a coordination complex at -70°C in CD_2Cl_2 in a NMR tube and monitored the spectrum as a function of temperature. The initial and final spectra allowed us to determine a relative displacement series. The following results were observed. The $UCl_4(dmpe)_2$ does not exchange with tmed at 28°C nor with diars. Conversely, dmpe quantitatively displaces diars or tmed from their respective coordination complexes with UCl_4. In a related pair of experiments $UCl_4(diars)_2$ was mixed with tmed and $UCl_4(tmed)_2$ with diars. In both cases resonances due to $UCl_4(tmed)_2$, free diars and free tmed were observed in the ^1H NMR spectrum. We also observed resonances due to a new set of resonances which we ascribe to coordinated diars and coordinated tmed, i.e., presumably due to $UCl_4(diars)(tmed)$. Therefore the equilibria shown in eq. (1) and (2) are established. From the

$$UCl_4(diars)_2 + tmed \overset{K_1}{=} UCl_4(diars)(tmed) + diars \qquad (1)$$

$$UCl_4(diars)(tmed) + tmed \overset{K_2}{=} UCl_4(tmed)_2 + diars \qquad (2)$$

integrated intensity of the various species present in the spectrum K_2 is 0.9 at 19°C and K_1 is large.

These studies do not allow us to calculate all equilibrium constants since the K's are commonly very small or very large. Qualitatively, however, we have been able to establish that for the reference acid UCl_4, the coordinative affinity is dmpe > tmed > diars.

The displacement equilibria are slightly more complex for $ThCl_4$(bidentate ligand)$_2$ when compared to their uranium analogues. The diarsine ligand in $ThCl_4(diars)_2$ is completely displaced by $Me_2PCH_2CH_2PMe_2$. Conversely, the diarsine will not displace dmpe in $ThCl_4(dmpe)_2$. Thus, this displacement series, dmpe > diars, is analogous to that found in uranium. However, mixing $ThCl_4(tmed)_2$ with $Me_2PCH_2CH_2PMe_2$ or $ThCl_4(dmpe)_2$ with $Me_2NCH_2CH_2NMe_2$ gives an equilibrium mixture as defined by equations 3 and 4. Using

$$ThCl_4(dmpe)_2 + tmed \overset{K_1}{=} ThCl_4(dmpe)(tmed) + dmpe \qquad (3)$$

$$ThCl_4(dmpe)(tmed) + tmed \overset{K_2}{=} ThCl_4(tmed)_2 + dmpe \qquad (4)$$

$^{31}P\{^1H\}$ NMR spectroscopy, the relative amounts of $ThCl_4(dmpe)_2$, δ -7.27, $ThCl_4(dmpe)(tmed)$, δ -5.69, and free dmpe, δ 47.42, may be estimated. Using the same solution the relative concentration of $ThCl_4(tmed)_2$ and free tmed may be determined by ^1H NMR spectroscopy. Thus, we can estimate K_1 and K_2 to be 0.25 and 0.86 at 23°C, respectively. For the acceptor $ThCl_4$ the relative coordination affinity is dmpe ≥ tmed > diars.

These studies show that chelating, alkyl-phosphines are very good ligands for UCl_4, and they are significantly better ligands than amines or arsines. The reasons for this could be steric, since the crystal structure of $UCl_4(tmed)_2$ shows significant distortion due to intramolecular repulsion. This study has concentrated upon chelate ligands and complications due to entropy and ring strain cannot be readily evaluated. In future we intend to design systems with monodentate ligands so that some of these difficulties will be overcome.[15]

Crystal Structure of $UCl_4(diars)_2$. An ORTEP drawing of $UCl_4(diars)_2$ is shown in Figure III. Positional parameters are in Table I, bond length and bond angles are in Table II, and crystal data are in Table IV. The uranium atom is located on a special position, $\bar{4}2m$ in the space group. The geometry of the complex is related to a dodecahedron with the arsenic atoms on the A-sites and the chloride atoms on the B-sites.[16] The distortion away from idealized dodecahedral symmetry can be described in terms of the shape parameters, δ' and ϕ as defined in ref. 17. The shape parameters for $UCl_4(tmed)_2$, $U(OPh)_4(dmpe)_2$, and $UCl_4(diars)_2$ are listed in Table III.

The U-Cl distance of 2.618(3)Å is similar to that of 2.609 ± 0.009Å found in $UCl_4(tmed)_2$.[6] The U-As distance of 3.049(1)Å is unique, though it is in the region expected since the Nb-As distance in $NbCl_4(diars)_2$ is 2.732(8)Å[18] and the radius of Nb(IV) in eight coordination is estimated to be 0.21Å shorter than that of U(IV) in eight coordination.[19] It is of interest to note that the Nb-Cl bond distance of 2.515(1)Å in $NbCl_4(diars)_2$ is only 0.10Å shorter than the U-Cl bond

distance in $UCl_4(diars)_2$ whereas the Nb-As bond distance is 0.32Å shorter than the U-As bond distance. On average, the Nb(IV) radius in eight coordination is therefore 0.21Å smaller than that of U(IV), as predicted.[19]

Experimental Section

All operations were performed under argon. Elemental analyses were done by the microanalytical laboratory of this department. Proton, carbon, and phosphorus nuclear magnetic resonance spectra were recorded on a JEOL FX90 Q machine. Some proton spectra were recorded on the UCB-300 machine, operating at 300MHz.

$ThCl_4(Me_2PCH_2CH_2PMe_2)_2$

1,2-Bis(dimethylphosphino)ethane (6 mL, 0.036 mol) was added dropwise to thorium tetrachloride (4.3g, 0.0012 mol) at 0°C with stirring. The suspension was warmed to room temperature then heated to 80°C for 24 h. The mixture was cooled to room temperature, the solid was washed with pentane (2 x 10 mL) and the white residue was extracted with dichloromethane (2 x 30 mL). The combined extracts were concentrated to saturation then cooled to -20°C. The colorless prisms were collected, washed with pentane (2 x 10 mL) and dried under reduced pressure. A second crop of crystals was obtained from the mother liquor, the combined yield was 5.2g (67%). When heated in a sealed capillary, the complex did not melt to 360°C. The analytical and NMR data are in footnote 8 of reference 1b. IR (Nujol mull): 1415m, 1291m, 1272m, 1161w, 1150w, 1120w, 1080m, br, 965w, 946s, 921m, 884w, 858w, 821w, 720w, 691m, 638w, 622w, and 233s cm^{-1}.

$ThI_4(Me_2PCH_2CH_2PMe_2)_2$

1,2-Bis(dimethylphosphino)ethane (0.7 mL, 0.0042 mol) was added to thorium tetraiodide (1.0g, 0.0014 mol) in dichloromethane (20 mL). The supernatant liquid slowly turned pink as the thorium tetraiodide dissolved over 12 hr. The volatile material was evaporated and the pink

residue was crystallized from a minimum amount of dichloromethane in 72% (1.0g) yield. The complex does not melt to 360°C. The analytical and NMR spectral data are reported in footnote 6 in reference 1b. IR: 1415m, 1299m, 1281m, 1170w, 1137m, 1088w, 1000w, 949s, 931s, 896m, 869m, 837w, 803w, 732s, 702s, and 643s cm^{-1}.

$\underline{UCl_4(Me_2PCH_2CH_2PMe_2)_2}$

To a suspension of uranium tetrachloride (5.8g, 0.015 mol) in dichloromethane (50 mL) was added 1,2-bis(dimethylphosphino)ethane (8mL, 0.048 mol). The supernatant liquid became blue-green within minutes and the suspension was stirred for 12 h. The solution was filtered, the filtrate was concentrated to saturation and cooled (-20°C). The green prisms were collected, washed with pentane (2 x 5 mL) and dried under reduced pressure. The mother liquor and combined washings were cooled (-70°C) to give a second crop of crystals in combined yield of 89% (9.3g). The complex may be crystallized from toluene (-20°C). The complex is soluble in halogenated and aromatic hydrocarbons and slightly soluble in aliphatic hydrocarbons and diethyl ether. The complex decomposes at 315°C without melting. The analytical and NMR spectral data are in footnote 3 of reference 1b. The infrared spectrum is virtually superimposable upon that of $ThCl_4(dmpe)_2$, except that ν U-Cl appears at 245(s) cm^{-1}. The complex may be crystallized from diethylether or tetrahydrofuran without change. Heating in vacuum to 160°C does not liberate the coordinated phosphine.

$\underline{UBr_4(Me_2PCH_2CH_2PMe_2)_2}$

This complex was prepared in a manner analogous to $UCl_4(dmpe)_2$ in 78% yield. The analytical and NMR spectral data are reported in

footnote 5 of reference 1b. The infrared spectrum is superimposable upon that of $UCl_4(dmpe)_2$ with the exception that no absorptions were observed below 641 cm^{-1}.

$\underline{UCl_4(Me_2NCH_2CH_2NMe_2)_2}$

To a suspension of uranium tetrachloride (1.0g, 0.0026 mol) in toluene (20 mL) cooled to -20°C was added the diamine (1.0g, 0.0086 mol). After warming to room temperature the suspension was stirred until a homogeneous solution was obtained, ca. 4h. The green solution was filtered and the volume of the filtrate was reduced to saturation. Cooling (-20°C) gave large, green prisms which were collected, washed with pentane (5 mL) and dried under reduced pressure to yield 1.3g (85%) of an amorphous powder, mp 180°C (dec.). The complex is soluble in halogenated and aromatic hydrocarbons and slightly soluble in aliphatic hydrocarbons and diethyl ether. The diamine is displaced by tetrahydrofuran to give a complex that we have not characterized. Anal. Calcd for $C_{12}H_{32}Cl_4N_4U$: C, 23.5; H, 5.27; H, 9.15. Found: C, 23.1; H, 5.41; N, 9.08. IR: 1301m, 1281m, 1236m, 1185w, 1167m, 1119m, 1101m, 1076m, 1040m, 1011s, 1002s, 989m, 949s, 917m, 791s, 782m, 720m, br, 596m, 494m, br, 458m, br, and 374m cm^{-1}.

$\underline{ThCl_4(Me_2NCH_2CH_2NMe_2)_2}$

The complex was prepared in a manner similar to that of its uranium analogue and crystallized from toluene (-20°C) as colorless prisms in 80% yield, mp 210°C (dec.). Anal. Calcd for $C_{12}H_{32}Cl_4N_4Th$: C, 23.8; H, 5.32; N, 9.24; Cl, 23.4. Found: C, 23.9; H, 5.23; N, 9.19; Cl, 22.8. The infrared spectrum is essentially identical to that of $UCl_4(tmed)_2$.

$\underline{UCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2}$

1,2-Bis(dimethylarsine)benzene (1.9g, 0.0066 mol) was added to uranium tetrachloride (1.0g, 0.0026 mol) and the mixture was stirred for 3d, giving a blue-grey suspension. The suspension was extracted with dichloromethane (5 x 20 mL) and the combined extracts were concentrated to ca. 50 mL and cooled (-20°C). The pale blue-violet prisms (2.0g, 81%) were collected and dried under reduced pressure, mp 160°C (dec.). Anal. Calcd for $C_{20}H_{32}As_4Cl_4U$: C, 25.2; H, 3.36; Cl, 14.9. Found: C, 24.5; H, 3.34; Cl, 14.8. IR: 3160w, br, 1303w, 1270m, 1247w, 1236w, 1210w, 1168m, 1147m, 1121m, 1090m, 1028m, 970m, br, 902s, 871s, 846m, 757s, 723s, 602s, 445s, and 257s cm^{-1}. The complex is insoluble in aliphatic hydrocarbons and diethyl ether and slightly soluble in halogenated hydrocarbons and tetrahydrofuran. Crystallization of $UCl_4(diars)_2$ from tetrahydrofuran gives $UCl_4(diars)(thf)_2$. Anal. Calcd for $C_{18}H_{32}As_2Cl_4O_2U$: C, 26.7; H, 3.95; Cl, 17.5. Found: 25.7; H, 3.76; Cl, 16.4

$ThCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$

Thorium tetrachloride (1.0g, 0.0027 mol) and the diarsine (1.9g, 0.0066 mol) were mixed and the mixture was heated to 90°C for 3d. The pale grey suspension was cooled to room temperature and extracted with dichloromethane (5 x 20 mL). The combined extracts were concentrated to ca. 50 mL and cooled (-20°C). The colorless prisms (1.9g, 76% yield) were collected and dried under reduced pressure. The complex decomposed at ca. 200°C without melting. Anal. Calcd for $C_{20}H_{32}As_4Cl_4Th$: C, 25.4; H, 3.41; Cl, 15.0. Found: C, 25.7; H, 3.44; Cl. 14.4. The infrared spectrum is essentially identical to that of its uranium analogue.

$UCl_4[Me_2PCH_2CH_2PMe_2][Me_2NCH_2CH_2NMe_2]$

To a solution of $UCl_4(tmed)_2$ (1.2g, 0.0020 mol) in dichloromethane (20 mL) at -40°C was added 1,2-bis(dimethylphosphino)ethane (0.3 mL, 0.0020 mol) and the solution was stirred at -30°C for 1 h. The light green solution was filtered rapidly and the filtrate was concentrated at -40°C to ca. 5 mL. Pentane (ca. 5 mL) was added, followed by rapid filtration and cooling to -80°C. The bright green prisms were collected (-40°C) and washed with cold (-40°C) pentane (5 mL) and dried under reduced pressure, mp 90°C (dec.). The yield was essentially quantitative. The dry crystals were stable at 20°C for at least two weeks though solutions decompose above -20°C. For spectroscopic studies, the complex was dissolved in solvents cooled to -70°C and the solutions were never allowed to warm above -30°C. ^1H NMR (CD_2Cl_2,-30°C): δ 11.9 (6H)s, Me_2N; 2.90 (6H)s, Me_2P; 1.90 (6H)s, PMe_2; -20.6 (6H)s, Me_2N; -23.6 (2H)s, PCH_2; -36.5 (2H)s, PCH_2; -37.1 (2H)s, CH_2N; -56.2 (2H)s, CH_2N. Anal. Calcd for $C_{12}H_{32}Cl_4N_2P_2U$: C, 22.3; H, 4.99; N, 4.34; P, 9.59; Cl, 21.9. Found: C, 22.2; H, 5.45; N, 4.29; P, 9.60; Cl, 21.5.

Collection and Reduction of X-Ray Data

Light blue crystals of the complex were mounted in quartz capillaries under nitrogen. A crystal selected for X-ray analysis was centrifuged into the narrow tip of the capillary. Lattice parameters were refined from 24 selected reflections <13° < 2θ < 32°) by using the Enraf-Nonius CAD-4 automatic centering and least-squares routines.[20] Systematic absences are consistent with space groups D_{2d}^{9} - $I\bar{4}m2$ and D_{2d}^{11} - $I\bar{4}2m$. The latter was assumed and confirmed by successful solution

and refinement of the structure. Crystal and data collection parameters are listed in Table IV. Intensity data were collected on a CAD-4 automated diffractometer to $2\theta=55°$ by using the $\theta-2\theta$ scan mode and a scan range determined by $\Delta\theta=(0.50+0.347\tan\theta)°$ with an additional $0.25(\Delta\theta)$ at both ends of the scan for background measurements. The intensities of three standard reflections measured every 2 hr. showed only random statistical fluctuations (±1%) over the period of data collection. The data (4 sets) were corrected for Lorentz, polarization, absorption and merged (R=2.7%). Of the 556 unique reflections, 525 have $F_o^2 > 2\sigma(F_o^2)$ and were used for solution and refinement of the structure.[21] Neutral atom scattering factors were obtained from standard tables.[22a] Anomalous dispersion corrections were applied to uranium and arsenic atoms.[22b]

Solution and Refinement of the Structure

$UCl_4(diars)_2$ is situated in space group $I\bar{4}2m$ such that one fourth (7 atoms) of the molecule constitute the asymmetric unit (the uranium atom is located on a $\bar{4}2m$ site; all nonhydrogen atoms, except the methyl-carbon atoms, are on the mirror plane x,x,z).

The structure was solved by Patterson and Fourier methods and refined[23] by full matrix least-squares procedure. The positions of the uranium and arsenic atoms were obtained through a three-dimensional Patterson synthesis. Four cycles of isotropic least-squares refinement (R=0.16) followed by a difference Fourier map revealed the positions of all nonhydrogen atoms. Subsequent anisotropic refinement minimizing $\Sigma w(|F_o|-|F_o|)^2$, where $w=1/\sigma^2(F_o)$, converged to a final residual index of $R_f(F_o) = 0.020$ and $R_{wf}(F_o) = 0.027$. The R index for all data is 0.025.

No correction for extinction[24] was applied. The final difference map revealed no additional chemical features in the unit cell.

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(6) The phosphine complex $UCl_4(dmpe)_2$, orthorhombic, $P2_12_12_1$, a = 13.870(3)A, b = 42.304(7)A, c = 13.001(3)A, V = 7628A^3, z = 12[b], is isostructural with $UCl_4(tmed)_2$, orthorhombic, $P2_12_12_1$, a = 13.094(4)A, b = 13.265(4)A, c = 12.633(4)A, V = 2199A,^{3} z = 4.[c] The X-ray structure of the amine complex has been solved and the chloride ligands are on the B-sites and the nitrogen atoms are on the A-sites in a D_{2d}-dodecahedron. (b) Zalkin, A. personal communication. (c) Zalkin,A.; Edwards, P.G.; Zhang, D.; Andersen, R.A. submitted to Acta Cryst.

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(10) The simulated spectrum of the free ligand gave the values, $\delta A = \delta A' = 7.33$, $\delta B = \delta B' = 7.14$, $J_{AB} = 7.85$ Hz, $J_{BB'} = 7.0$ Hz, $J_{A'B} = 1.2$ Hz, and $J_{AA'} = 0.5$ Hz.

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(20) Intensity data were collected at CHEXRAY-University of California Chemistry Department Crystallographic Facility. The reduction formulae standard for the CAD-4 system are as follows: The net intensity I = w/NPI(C-2B), where w=20.1166x(attenuator factor, x was 18.2 when set), NPI = ratio of the maximum scan rate to scan rate for the measurement, C = total scan count, and B = total background count. $\sigma(F_o^2)$ =

w/Lp.NPI[C+4B + $(PI^2)^2$]1/2, where P = 0.06 is a factor used to lower the weight of intense reflections. $\sigma(Fo) = \sigma(F_o^2)/2F_o$.

(21) An empirical absorption correction (μ = 96.6 cm^{-1}) was applied using psi-scans of five reflections having 2θ values between 13 and 30.

(22) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1975: Vol. IV; (a) Table 2.2A, pp. 72-98; (b) Table 2.3.1, pp. 149-150.

(23) All crystallographic computing was performed on a CDC Cyber 170/750 computer at California State University, Data Center, LA, using CRYSYS a system of computer programs which include CRYGLS, a modified version of Martin-Busing-Levy group least-squares program; FOURMAPS - Fourier program incorporating XFFT and SEARCH of MULTAN; modified version of C.K. Johnsons ORTEP and other programs developed and adapted for the CDC system by one of us (RWG).

(24) Three strong reflections 101, 110 and 006 indicated secondary extinction effects and were excluded from the final cycles of refinement.

Acknowledgement

This work is supported by the Director, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. We thank Dr. F.J. Hollander of the CHEXRAY facility, University of California, Berkeley for collecting the X-ray data and Professor C.J. Hawkins, Dr. J.G. Brennan and Dr. K. Smith for stimulating discussions on fluxional processes in eight coordination.

Supplementary Material Available. Listing of Structure Factor Tables (4 pages). Ordering information is given on any current masthead.

Table I.

Positional Parameters for $UCl_4(diars)_2$

Atom	X	Y	Z
U1	0.00000	0.00000	0.00000
As	0.12537(11)	0.12537(11)	-0.14739(5)
CL	0.18907(32)	0.18907(32)	0.04203(16)
CM	0.1087(11)	0.3305(8)	-0.1608(5)
C1	0.0525(11)	0.0525(11)	-0.2444(4)
C2	0.1028(14)	0.1028(14)	-0.3157(5)
C3	0.0500(13)	0.0500(14)	-0.3844(5)

Table II

Some Selected Bond Lengths (Å) and Bond Angles (deg) in $UCl_4(diars)_2$

U-As	3.049(1)
As-C(M)	1.950(7)
As-C(1)	1.939(8)
C(1)-C(2)	1.405(12)
C(2)-C(3)	1.381(14)
C(3)-C(3')	1.331(18)
Cl(1)-U-Cl(2')	147.72(9)
Cl(1)-U-Cl(2)	94.43(9)
As(1)-U-As(1')	66.32(3)
As(1)-U-As(2)	134.49(3)
Cl(1')-U-As(1')	76.54(7)
Cl(2')-U-As(1')	72.98(6)
Cl(2)-U-As(1')	139.30(6)
C(M)-As-C(M)	98.31(36)
C(1)-As-U	116.85(28)
C(M)-As-U	116.83(26)
As-C(1)-C(1')	120.00(56)

Table III. Shape Parameters

Compound	δ'(deg)	ϕ(deg)
$UCl_4(tmed)_2$	20.4,21.9,38.7,39.6	1.6
$UCl_4(diars)_2$	24.1, 24.1, 24.1, 24.1	0
$U(OPh)_4(dmpe)_2$	13.0,15.5,8.26,11.1	1.7
Idealized dodecahedron (D_{2d})	29.5, 29.5, 29.5, 29.5	0
Idealized bicapped trigonal prisms (C_{2v})	0,21.8,48.2,48.2	14.1
Idealized square antiprism(D_{4h})	0,0,52.4,52.4	24.5

Table IV.

Crystallographic data for the X-ray diffraction study of $UCl_4(diars)_2$

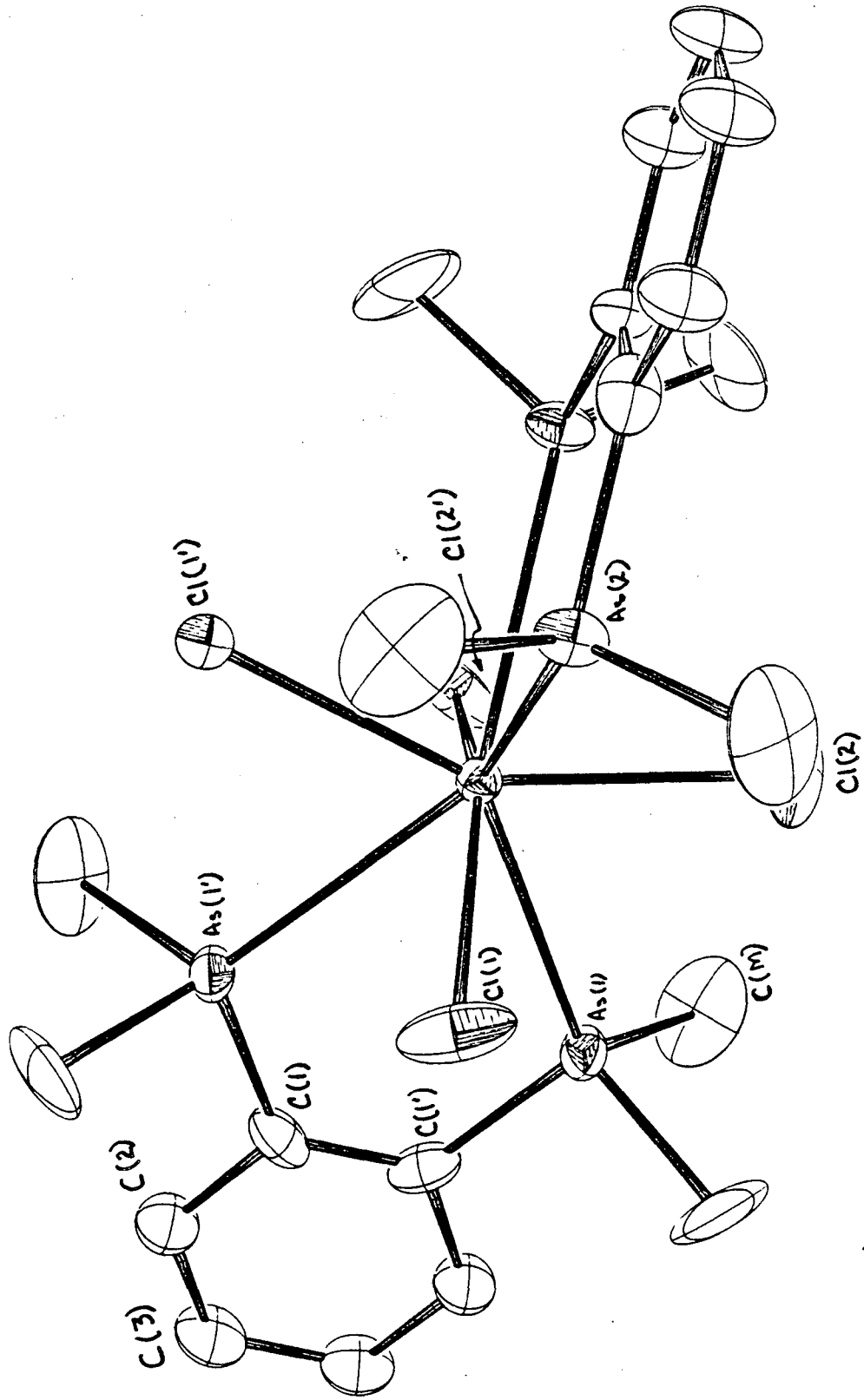
formula	$UAs_4Cl_4C_{20}H_{32}$
temp. °0 (±3°C)	25
fw	952.01
space group	$I\bar{4}2m$
a, A	9.407(1)
c, A	17.318(2)
V, A^3	1532.5
Z	2
d(calcd), g/cm^3	2.063
d(obsd), g/cm^3	2.07
crystal size, mm	0.3 x 0.3 x 0.2
crystal decomposition, %	0
x-ray exposure time, h	53
μ(Mo Kα), cm^{-1}	96.58
radiation	Mo $K\bar{\alpha}$ (0.71073A).
monochromator	graphite
detector aperture, mm	
horizontal (A + Btanθ)	
A	2.0
B	1.0
vertical	3.0
collection range	+h ±k ±1, 3° ≤ 2θ ≤ 55°
scan type	θ-2θ

scan width ($\Delta\theta$), deg.	$0.50 + 0.347\tan\theta$
θ-scan rate (variable	
max, deg/min	6.7
min. deg/min	0.69
no. of unique data	556
no. of data $Fo^2 > 2\sigma(Fo^2)$	525
P	0.06
no. of variables	42
R(Fo) (b)	0.020
Rw(Fo) (b)	0.027
esd in observn of unit wt.	1.24
largest shift/error value	
on final cycle	0.02
largest peak in final diff	
Fourier, $e/Å^3$	0.93

(a) The observed density was obtained by flotation in a CCl_4/CH_2Br_2 mixture.

(b) $R_F(F_o) = \Sigma\ |F_o| - |F_o|/\Sigma\ F_o$, $R_{WF}(F_o) = [\Sigma w<|F_o|-|F_o|>^2/\Sigma w|F_o|^2]11/2$

Figure III. ORTEP diagram of $UCl_4(diars)_2$; 50% probability ellipsoids.



Supplementary Material For

Preparation of $MCl_4(Me_2ECH_2CH_2EMe_2)_2$ and $MCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$ where M is Thorium or Uranium and E is Nitrogen or Phosphorus.

Crystal Structure of $UCl_4[(1,2\text{-}Me_2As)_2C_6H_4]_2$.

Peter G. Edwards, Richard A. Andersen, and Robert W. Gellert

Structure Factor Tables and Thermal Parameters (4 pages)

Anisotropic Thermal Parameters

Atom	U11	U22	U33	U12	U13	U23
U	0.00650(7)	0.00650(7)	0.00156(2)	0	0	0
As	0.0085(11)	0.0085(11)	0.00190(3)	-0.00234(6)	0.00011(5)	0.00011(5)
C1	0.0132(4)	0.0132(4)	0.00325(9)	-0.0058(2)	-0.00073(2)	-0.00073(2)
CM	0.0239(14)	0.0076(7)	0.0038(3)	-0.0033(7)	-0.0007(5)	0.0005(4)
C1	0.0090(10)	0.0090(10)	0.0016(2)	-0.0014(6)	0.00008(5)	0.00008(5)
C2	0.012(1)	0.012(1)	0.0021(3)	-0.0003(8)	0.0011(7)	0.0011(3)
C3	0.013(1)	0.013(1)	0.0017(2)	-0.0003(8)	0.0007(6)	0.0007(6)

OBSERVED AND CALCULATED STRUCTURE FACTORS OF
UCL4(DIARS)2 COMPLEX

H	K	L	10 X FOBS	10 X FCAL	PHASE ANGLE	H	K	L	10 X FOBS	10 X FCAL	PHASE ANGLE	H	K	L	10 X FOBS	10 X FCAL	PHASE ANGLE
2	0	0	1187	1108	9	11	4	1	651	699	8	3	2	3	1575	1564	27
4	0	0	1060	878	178	6	5	1	1352	1202	50	5	2	3	634	660	-15
6	0	0	1146	1140	8	8	5	1	228	228	68	7	2	3	988	838	-15
8	0	0	1438	1313	11	10	5	1	669	686	-15	9	2	3	835	811	34
10	0	0	644	634	11	7	6	1	721	699	58	11	2	3	418	448	23
1	1	0	3078	3397	4	9	6	1	628	656	-11	4	3	3	198	215	-51
3	1	0	600	464	13	8	7	1	838	856	10	6	3	3	871	760	-5
5	1	0	365	347	17	9	8	1	548	621	8	8	3	3	1473	1324	11
7	1	0	1328	1177	10	0	0	2	539	768	10	10	3	3	455	468	27
9	1	0	1065	979	10	2	0	2	561	512	20	5	4	3	125	80	-58
2	2	0	2232	2052	5	4	0	2	1978	1804	7	7	4	3	1595	1425	17
4	2	0	1295	1240	8	6	0	2	1214	1218	7	9	4	3	962	942	4
6	2	0	676	687	13	8	0	2	322	288	23	11	4	3	120	122	38
8	2	0	891	787	10	10	0	2	732	672	11	6	5	3	1308	1128	25
10	2	0	334	350	19	12	0	2	505	552	13	8	5	3	904	892	8
12	2	0	344	378	16	1	1	2	1365	1245	51	10	5	3	387	419	-2
3	3	0	2654	2441	5	3	1	2	1644	1579	51	7	6	3	594	570	14
5	3	0	1240	1252	10	5	1	2	1661	1641	-19	9	6	3	382	405	0
7	3	0	446	416	13	7	1	2	1056	858	-37	8	7	3	140	175	14
9	3	0	164	150	32	9	1	2	819	759	50	9	8	3	139	150	8
11	3	0	541	575	14	11	1	2	645	675	31	0	0	4	414	335	171
4	4	0	2514	2457	7	2	2	2	1722	1787	41	2	0	4	947	1021	10
6	4	0	1013	865	10	4	2	2	1138	1078	17	4	0	4	2581	2626	6
8	4	0	262	230	170	6	2	2	1366	1377	-54	6	0	4	981	960	9
10	4	0	426	422	16	8	2	2	1039	923	11	8	0	4	323	232	166
5	5	0	2141	1806	6	10	2	2	932	893	60	10	0	4	653	609	12
11	5	0	745	791	11	3	3	2	1450	1418	26	12	0	4	659	724	12
6	6	0	642	595	12	5	3	2	899	858	-61	1	1	4	1433	1512	-63
8	6	0	478	495	15	7	3	2	1265	1080	-6	3	1	4	1662	1746	0
10	6	0	667	691	11	9	3	2	930	870	35	5	1	4	1757	1782	26
7	7	0	886	850	11	11	3	2	352	404	40	7	1	4	289	268	16
9	7	0	862	924	10	4	4	2	501	474	-37	9	1	4	299	293	12
8	8	0	1135	1165	9	6	4	2	1016	874	14	11	1	4	714	711	-1
1	0	1	2161	2537	5	8	4	2	933	861	15	2	2	4	1619	1634	-22
5	0	1	918	863	7	10	4	2	471	510	9	4	2	4	1101	1119	24
7	0	1	1335	1188	10	5	5	2	1163	973	40	6	2	4	903	780	38
9	0	1	1038	973	10	7	5	2	977	906	42	8	2	4	856	771	10
11	0	1	331	344	14	9	5	2	627	634	-14	10	2	4	594	590	-17
2	1	1	1838	1715	67	11	5	2	417	466	-15	3	3	4	780	794	-14
4	1	1	824	766	52	6	6	2	1242	1098	54	5	3	4	372	362	69
6	1	1	1395	1387	-31	8	6	2	425	432	8	7	3	4	1395	1205	19
8	1	1	1158	1019	7	10	6	2	579	634	-30	9	3	4	952	936	-5
10	1	1	793	773	46	7	7	2	399	426	26	4	4	4	464	482	-129
3	2	1	2287	2168	43	9	7	2	459	486	-17	6	4	4	1019	917	23
5	2	1	1031	973	-34	8	8	2	382	432	0	8	4	4	1317	1274	5
7	2	1	1218	1039	-22	1	0	3	522	519	9	10	4	4	420	432	4
9	2	1	920	845	43	3	0	3	1671	1796	8	5	5	4	618	556	-17
11	2	1	461	496	48	5	0	3	2461	2387	6	7	5	4	1088	1034	-3
4	3	1	1703	1597	18	7	0	3	113	109	138	9	5	4	698	709	17
6	3	1	969	822	-31	11	0	3	929	952	10	6	6	4	1057	967	-25
8	3	1	628	569	14	2	1	3	1439	1383	7	8	6	4	462	470	11
10	3	1	588	585	53	4	1	3	2204	2177	18	10	6	4	506	553	55
5	4	1	1380	1411	9	6	1	3	811	838	-24	7	7	4	305	323	-12
7	4	1	533	470	36	10	1	3	746	707	30	9	7	4	394	408	60
9	4	1	217	219	33	12	1	3	568	645	8	8	8	4	234	231	67

OBSERVED AND CALCULATED STRUCTURE FACTORS OF
UCL4(DIARS)2 COMPLEX

H	K	L	10 X FOBS	10 X FCAL	PHASE ANGLE
1	0	5	1156	1397	7
3	0	5	1329	1353	7
5	0	5	1197	1130	8
7	0	5	758	648	12
9	0	5	603	489	15
11	0	5	469	448	15
2	1	5	2016	2204	-51
4	1	5	1386	1420	24
6	1	5	1419	1163	46
8	1	5	611	529	26
10	1	5	612	596	-25
3	2	5	1504	1579	-25
5	2	5	1464	1496	58
7	2	5	1044	895	46
9	2	5	676	646	-20
11	2	5	501	519	-30
4	3	5	760	776	-2
6	3	5	1435	1214	61
8	3	5	818	769	15
10	3	5	644	636	-37
5	4	5	862	735	16
7	4	5	888	805	27
9	4	5	564	576	-9
11	4	5	418	456	27
6	5	5	931	859	-26
8	5	5	600	607	-3
10	5	5	611	661	51
7	6	5	840	808	-38
9	6	5	706	749	53
8	7	5	526	549	29
0	0	6	2071	2954	5
2	0	6	781	908	11
4	0	6	429	471	172
10	0	6	703	617	11
1	1	6	1661	1942	-34
3	1	6	526	525	-23
5	1	6	809	824	71
7	1	6	1409	1181	16
9	1	6	1123	1001	5
11	1	6	327	332	-23
2	2	6	1503	1574	-52
4	2	6	1044	1116	33
6	2	6	1387	1123	42
8	2	6	810	722	20
10	2	6	618	612	-22
3	3	6	1390	1375	-11
5	3	6	1683	1460	27
7	3	6	798	727	58
9	3	6	385	395	-35
11	3	6	586	628	-1
4	4	6	1701	1889	0
6	4	6	993	854	33
10	4	6	440	453	3
5	5	6	1396	1224	0
7	5	6	372	344	-25
9	5	6	282	299	41
6	6	6	766	715	-38
8	6	6	510	516	9
10	6	6	601	653	49
7	7	6	724	719	-10
9	7	6	665	742	38
8	8	6	703	777	24
1	0	7	1810	2225	7
5	0	7	236	215	160
2	1	7	886	998	5
4	1	7	569	598	99
6	1	7	1191	979	-24
8	1	7	1436	1291	5
10	1	7	575	556	35
3	2	7	927	929	29
5	2	7	1212	1024	-6
7	2	7	906	783	-14
9	2	7	607	580	27
11	2	7	420	451	19
4	3	7	1589	1785	0
6	3	7	985	863	-8
10	3	7	484	505	19
5	4	7	1824	1582	-3
7	4	7	188	159	68
6	5	7	581	549	30
10	5	7	477	497	8
7	6	7	481	497	1
9	6	7	529	537	16
8	7	7	801	801	14
0	0	8	1239	1486	9
2	0	8	1339	1580	6
4	0	8	542	560	11
1	1	8	1411	1665	22
3	1	8	1268	1358	50
5	1	8	917	785	-28
7	1	8	1171	1006	-26
9	1	8	818	768	48
11	1	8	315	337	50
2	2	8	1321	1449	51
4	2	8	968	1052	26
6	2	8	1545	1311	-44
8	2	8	502	463	18
10	2	8	771	764	62
3	3	8	1108	1261	35
5	3	8	1529	1330	-21
7	3	8	428	410	-12
9	3	8	462	476	53
11	3	8	501	534	29
4	4	8	1486	1301	-6
6	4	8	751	659	27
8	4	8	264	266	33
10	4	8	461	503	8
5	5	8	940	809	48
7	5	8	674	665	52
9	5	8	505	523	-15
6	6	8	885	849	59
8	6	8	591	589	10
7	7	8	668	650	18
9	7	8	491	550	-3
8	8	8	557	608	9
1	0	9	270	290	24
3	0	9	1378	1647	7
5	0	9	1244	1009	11
2	1	9	1165	1300	38
4	1	9	1182	1305	21
6	1	9	1041	875	-39
8	1	9	549	485	15
10	1	9	691	650	50
3	2	9	1067	1198	64
5	2	9	1237	1098	-25
7	2	9	881	772	-30
9	2	9	817	806	55
11	2	9	497	520	32
4	3	9	613	519	1
6	3	9	1073	950	-16
8	3	9	745	679	25
10	3	9	583	623	37
5	4	9	490	382	14
7	4	9	969	920	29
9	4	9	735	745	9
6	5	9	1018	945	57
8	5	9	812	838	14
10	5	9	363	388	-26
7	6	9	709	723	36
9	6	9	399	433	-21
0	0	10	938	1046	178
2	0	10	1087	1284	7
4	0	10	2370	2052	8
6	0	10	590	473	17
1	1	10	237	251	-9
3	1	10	1407	1625	14
5	1	10	1347	1134	9
7	1	10	367	326	-20
9	1	10	359	321	41
2	2	10	750	813	34
4	2	10	917	801	16
6	2	10	901	795	-8
8	2	10	532	466	15
10	2	10	571	594	18
3	3	10	263	237	95
5	3	10	575	496	-5
7	3	10	972	856	5
9	3	10	778	811	14
4	4	10	312	302	-149
6	4	10	735	677	19
8	4	10	1165	1173	10
10	4	10	394	399	7
5	5	10	201	175	57
7	5	10	994	991	14
9	5	10	660	684	5

OBSERVED AND CALCULATED STRUCTURE FACTORS OF
UCL4(DIARS)2 COMPLEX

H	K	L	10 X FOBS	10 X FCAL	PHASE ANGLE
6	6	10	671	652	16
8	6	10	492	517	10
7	7	10	279	281	25
1	0	11	126	132	135
3	0	11	2173	1925	6
7	0	11	359	376	13
2	1	11	1002	1125	-27
4	1	11	1626	1452	9
6	1	11	905	838	43
8	1	11	300	272	27
10	1	11	470	483	-16
3	2	11	791	723	-27
5	2	11	1204	1117	38
7	2	11	680	643	40
9	2	11	513	525	-16
4	3	11	219	186	24
6	3	11	962	874	39
8	3	11	745	752	12
10	3	11	550	588	-14
5	4	11	256	225	39
7	4	11	896	874	10
9	4	11	752	778	5
6	5	11	558	538	-25
8	5	11	894	929	4
7	6	11	678	663	-14
8	7	11	148	143	50
0	0	12	697	761	13
2	0	12	1314	1133	8
4	0	12	648	560	14
1	1	12	1193	1033	-28
3	1	12	1240	1124	-29
5	1	12	810	748	52
7	1	12	884	840	42
2	2	12	1456	1355	-57
4	2	12	814	754	2
6	2	12	1270	1174	54
8	2	12	399	408	23
10	2	12	605	619	-33
3	3	12	821	764	-44
5	3	12	1140	1081	32
7	3	12	585	592	48
9	3	12	444	452	-25
4	4	12	964	865	9
6	4	12	563	533	5
8	4	12	442	445	3
5	5	12	620	612	-28
7	5	12	654	632	-27
9	5	12	426	454	40
6	6	12	776	732	-46
8	6	12	469	506	8
7	7	12	479	494	-14
1	0	13	1836	1688	8
3	0	13	576	459	10
5	0	13	327	264	164
2	1	13	1106	1061	-5
6	1	13	745	661	43
8	1	13	928	900	9
3	2	13	724	645	-19
5	2	13	978	905	31
7	2	13	655	619	46
9	2	13	379	391	-21
4	3	13	1430	1332	16
6	3	13	830	768	29
5	4	13	1247	1166	13
6	5	13	370	400	-11
8	5	13	252	256	22
7	6	13	482	508	2
0	0	14	1440	1245	12
2	0	14	904	812	10
4	0	14	228	196	168
1	1	14	1278	1201	34
3	1	14	468	390	55
5	1	14	314	283	-23
7	1	14	1028	938	8
9	1	14	677	671	13
2	2	14	777	806	58
4	2	14	699	640	13
6	2	14	813	753	-3
8	2	14	420	421	7
3	3	14	1006	981	32
5	3	14	1193	1131	4
7	3	14	202	219	-13
9	3	14	256	264	47
4	4	14	1465	1396	19
6	4	14	466	478	8
5	5	14	678	658	32
7	5	14	287	307	47
6	6	14	482	516	55
1	0	15	858	741	12
3	0	15	720	647	11
2	1	15	1193	1084	54
4	1	15	522	513	-14
6	1	15	680	644	-20
8	1	15	623	631	9
3	2	15	706	712	52
5	2	15	954	911	-33
7	2	15	559	584	-20
4	3	15	814	762	5
6	3	15	759	775	-30
8	3	15	253	272	21
5	4	15	611	602	5
7	4	15	309	333	0
6	5	15	469	495	49
2	0	16	1008	845	9
1	1	16	917	816	54
3	1	16	1043	996	24
5	1	16	782	760	-12
2	2	16	1210	1124	58
4	2	16	614	597	-3
6	2	16	593	616	-25
8	2	16	317	364	17
3	3	16	545	531	55
5	3	16	464	453	-18
7	3	16	543	581	-12
4	4	16	263	244	58
6	4	16	440	485	3
5	5	16	345	401	48
6	6	16	632	668	51
3	0	17	1282	1190	10
2	1	17	709	649	27
4	1	17	1115	1092	0
6	1	17	553	540	27
3	2	17	581	573	10
5	2	17	564	523	13
7	2	17	399	443	23
6	3	17	430	437	11
6	5	17	402	450	10
0	0	18	237	209	21
2	0	18	651	569	13
1	1	18	410	399	-7
3	1	18	904	857	-17
5	1	18	713	718	29
2	2	18	767	784	-32
4	2	18	538	511	-1
6	2	18	729	741	62
3	3	18	396	409	-27
5	3	18	461	453	61
4	4	18	275	295	67
6	4	18	365	399	4
5	5	18	293	351	-11
1	0	19	849	730	11
2	1	19	592	568	-22
4	1	19	293	282	-4
6	1	19	638	663	54
3	2	19	669	656	-31
5	2	19	588	586	54
4	3	19	612	636	23
5	4	19	558	615	20
0	0	20	1458	1233	9
2	0	20	523	437	16
1	1	20	961	846	13
5	1	20	225	248	20
2	2	20	553	553	-1
4	2	20	462	446	2
3	3	20	762	804	5
1	0	21	1021	923	10
2	1	21	645	593	40
4	1	21	179	173	2
3	2	21	562	587	31
0	0	22	527	523	12
2	0	22	311	290	22
1	1	22	591	537	48

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LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720