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Preparation and Crystal Structure of the Eight-Coordinate Complexes, Uranium Tetrachloridebis[1,2-dimethylarsinobenzene], $UCl_4(diars)_2$, and Uraniumtetrachloridebis[1,2-dimethylphosphinobenzene], $UCl_4(diphos)_2$

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Abstract

Two eight-coordinate compounds with idealized D_{2d}-symmetry, $UCl_4(diars)_2$ and $UCl_4(diphos)_2$, the only f-metal complexes of these ligands, have been prepared and characterized by X-ray diffraction studies.

The coordination chemistry of the chelating, bidentate ligand diars, 1,2-dimethylarsinobenzene, has been studied extensively by Nyholm and others in d-transition metal chemistry since the first complexes of Pd(II) were described by Chatt and Mann.[1] The phosphorus analogue, diphos, 1,2-dimethylphosphinobenzene, has been studied less extensively since the first complexes were described by Chatt and Hart.[2] The properties of several diphos coordination compounds in the latter part of the d-transition series have been described.[3] In contrast, the f-transition metal complexes of these two ligands have been ignored. One brief mention of $UCl_4(diars)_2$ has been made; it is said to be insoluble in dioxane and acetonitrile and to have a X-ray diffraction powder photograph similar though not identical to that of $NbCl_4(diars)_2$.[4] In this communication we describe the synthesis and solid state crystal structure of the eight-coordinate uranium compounds $UCl_4(diars)_2$ and $UCl_4(diphos)_2$, and their solution properties.

Stirring 2.5 molar equivalents of diars and UCl_4 for 3 days gave a blue-grey suspension. The suspension was soluble in dichloromethane from which pale blue-grey prisms of $UCl_4(diars)_2$ were crystallized by cooling to -20°C, m.p. 160°C (decomp.).† The diarsine complex is insoluble in aliphatic hydrocarbons and slightly soluble in toluene and dichloromethane; dissolution in tetrahydrofuran followed by crystallization from that solvent gives $UCl_4(diars)(thf)_2$.† The diphosphine, $UCl_4(diphos)_2$,† was prepared by refluxing UCl_4 with 2.5 molar equivalents of the diphosphine in toluene for 12 h followed by crystallization from toluene at -20°C as blue-green prisms. The diphosphine complex does not melt to 300°C. It gives a molecular ion in the e.i. mass spectrum that is essentially identical to the simulated ion. It is slightly soluble in toluene and dichloromethane, and it may be recovered unchanged from tetrahydrofuran.

An ORTEP diagram of $UCl_4(diphos)_2$ is shown in the Figure I. The diarsine complex is isomorphous with the diphosphine; both molecules crystallize in the tetragonal space group $I\bar{4}2m$ with the uranium atom sitting on the $\bar{4}$ axis. Since the molecules are

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† All compounds reported gave satisfactory elemental analyses.

isomorphous, only one ORTEP diagram is shown. Some bond lengths and angles for both complexes are listed in the Figure Caption.†† The geometry of both eight-coordinate molecules is based upon a dodecahedron with idealized D_{2d}-symmetry with the phosphorus or arsenic atoms on the A-sites and the chloride atoms on the B-sites.[5] The nearly trivial deviation from idealized dodecahedral geometry is shown by the shape parameters in the Table. The unique U-Cl distance in each of the molecules is 2.627(1) Å and 2.618(3) Å, in the diphosphine and diarsine, respectively. These distances are essentially identical to each other and to the U-Cl distance in $UCl_4(Me_2NCH_2CH_2NMe_2)_2$ where the U-Cl distance is 2.609(9) Å.[6] The U-P distance of 2.981(1) Å is 0.068 Å shorter than the U-As distance of 3.049(1) Å. The only other structural comparison between diars and diphos complexes with which we are familiar is the low-spin Co(III) complexes trans-$[CoCl_2(diphos)_2]ClO_4$[7] and trans-$[CoCl_2(diars)_2]Cl$,[8] in which the Co-Cl distances are identical, but the Co-P distance is 0.083 Å longer than the Co-As distance. The U-P(diphos) distance in $UCl_4(diphos)_2$ is 0.123 Å shorter than the U-P(dmpe) distance of 3.104(6)Å in $U(OPh)_4(Me_2PCH_2CH_2PMe_2)_2$.[9] Perhaps this is in part due to the larger size of phenoxide relative to chloride since in the only other structural comparison between these two phosphines, viz., high spin trans-$[MnBr_2(Me_2PCH_2CH_2PMe_2)_2]$[10a] and high spin trans-$[MnCl_2(diphos)_2]$,[10b] the Mn-P(diphos) distance is 0.030 Å longer than the Mn-P(dmpe)

†† Crystal data: $C_{20}H_{32}Cl_4P_4U$, M = 776.2, tetragonal, space group $I\bar{4}2m$, a = 9.188(1)Å, c = 17.064(2)Å, Z=2, U = 1440.5(7)Å^3, D_c = 1.79 g cm^{-3}, (Mo-Kα) radiation, λ = 0.71073Å, μ(Mo-Kα) = 59.4 cm^{-1}, T = -75°C. The structure was solved by a combination of Patterson and Fourier methods. Data were measured on a CAD4 diffractometer (2θ max. 55°). An empirical absorption correction was applied to the data and the correct enantiomorph was established by refining each against the data. In the difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of all of the hydrogen atoms. The hydrogen atoms were included and refined with isotropic thermal parameters. The final residuals for 60 variables refined against 519 observed [$F_0^2 > 3\sigma(F_0)^2$] data were R = 0.0138, Rw = 0.0153, and GOF = 0.918. $C_{20}H_{32}As_4Cl_4U$, M = 952.0, tetragonal, space group $I\bar{4}2m$, a = 9.407(1)Å, c = 17.318(2)Å, Z=2, U = 1532.5Å^3, D_c = 2.06 g cm^{-3}, D_m = 2.07 g cm^{-3}, (Mo-Kα) radiation, λ = 0.71073Å, μ(Mo-Kα) = 96.6 cm^{-1}, T = 25°C. The structure was solved by a combination of Patterson and Fourier methods. Data were measured on a CAD4 diffractometer (2θ max. 55°). An empirical absorption was applied to the data, and the correct enantiomorph was established by refining each against the data, and all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not located. The final residuals for 42 variables refined against 525 observed [$F_0^2 > 2\sigma(F_2^0)^2$] data were R = 0.020 and Rw = 0.027. Atomic coordinates, bond lengths and angles, thermal parameters, observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

distance. Thus the U-P distance in $UCl_4(diphos)_2$ is substantially shorter and presumably stronger than the U-As bond in $UCl_4(diars)_2$.

The ^1H NMR chemical shifts of $UCl_4(diphos)_2$ and $UCl_4(diars)_2$ are identical to within ±0.5 ppm in C_7D_8 and CD_2Cl_2 at 30°C.††† In addition the ^1H NMR resonances of both compounds in both solvents follow Curie law behaviour from -90°C to +110°C in C_7D_8 and from -90°C to + 30°C in CD_2Cl_2, i.e., the chemical shifts are linear in $T^{-1}(K)$. The ^1H NMR spectroscopic behaviour of the two compounds are different in tetrahydrofuran; the chemical shifts and their change as a function of temperature for $UCl_4(diphos)_2$ are identical to those found in toluene or dichloromethane. In contrast, the chemical shifts of $UCl_4(diars)_2$ in C_4D_8O differ from those found in the other two solvents††† and a plot of the chemical shift vs. $T^{-1}(K)$ is non-linear. This indicates that a temperature dependent equilibrium is present in solution and that the population of the individual species present in solution is changing as a function of temperature, giving rise to averaged chemical shifts that are non-linear in temperature. The identity of the species that are contributing to the solution equilibria are not known, though cooling a concentrated solution of $UCl_4(diars)_2$ in tetrahydrofuran yields $UCl_4(diars)(thf)_2$ as noted above, suggesting that this is one of the species present in thf solution.

A solution of $UCl_4(diphos)_2$ in C_7D_8 does not exchange with added diphos at temperatures up to 110°C since the ^1H NMR spectrum shows the unperturbed resonances of both molecules and a plot of δ vs. $T^{-1}(K)$ is identical to that observed in C_7D_8 without added diphos. The $UCl_4(diars)_2$ behaves similarly, i.e., added diars does not exchange

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††† In $UCl_4(diars)_2$ in PhMe-d_8 (+30°C) the Me_2As resonance is a singlet at δ+1.73 and the AA'BB' ring protons appear as a pair of four-line patterns at δA = + 0.68 and δB = - 4.19 with J_{AB} = 8Hz, $J_{BB'}$ = 7Hz, and $J_{AB'}$ = 1.2 Hz. In $UCl_4(diphos)_2$ the Me_2P resonance is a singlet at δ+2.46 and the pair of four-line patterns appear at δA = +1.12 and δB = -3.84 with coupling constants similar to those in the diarsine. The linewidths are similar to those of the protio-toluene in PhMe-d_8. In C_4D_8O at 28°C, the only resonance observed for $UCl_4(diars)_2$ is a single line at δ1.24 due to the Me_2As protons; the ring methyne protons are presumably broadened by chemical exchange since at -16°C, the Me_2As resonance is a singlet at δ 1.05 and the ring protons appear as four-line multiplets with δA = +0.92 and δB = -4.33. In C_7D_8 at 30°C, methyl resonances for $UCl_4(diphos)(diars)$ appear at δ+2.57 and +1.45 and the ring methyne protons appear at δ+1.04, +0.60, -3.19, and -5.14.

with coordinated diars up to 110°C. Thus, bidentate ligand exchange (eqs. 1) is slow on an NMR time scale. However, mixing approximately equal amounts of $UCl_4(diphos)_2$ and $UCl_4(diars)_2$ in C_7D_8 at 30°C initially gives ^1H NMR resonances due to the individual species, but with time new resonances due to the mixed species $UCl_4(diphos)(diars)$[†††] appear in amounts indicating statistical exchange after 24 h; the $t_{1/2}$ is ca. 3h. The cross-over exchange (eq. 2), which is slow on

$$UCl_4(diphos)_2 + diphos^* \not\rightleftharpoons UCl_4(diphos)(diphos^*) + diphos \qquad (1a)$$

$$UCl_4(diars)_2 + diars^* \not\rightleftharpoons UCl_4(diars)(diars^*) + diars \qquad (1b)$$

$$UCl_4(diphos)_2 + UCl_4(diars)_2 \rightleftharpoons 2UCl_4(diphos)(diars) \qquad (2)$$

an NMR time scale, shows that the bidentate ligands do indeed exchange in toluene solution. Studies of the exchange mechanism are in progress. In addition, diphos will quantitatively displace diars from $UCl_4(diars)_2$ in C_7D_8, though the inverse displacement does not occur on an NMR time scale. The solution spectroscopic studies mirror the solid state results since they show that diphos is a better ligand than diars towards UCl_4.

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References

1. (a) J. Chatt and F.G. Mann, J. Chem. Soc. **1939**, 1622. (b) E.C. Alyea, in "Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands," C.A. McAuliffe (ed.) John Wiley, New York 1973, p. 308. (c) W. Levason, Comments Inorg. Chem. **1990**, 9, 331.

2. (a) J. Chatt and F.A. Hart, J. Chem. Soc. **1960**, 1378. (b) R.J.H. Clark, R.H.U. Negrotti, and R.S. Nyholm, J. Chem. Soc. Chem. Comm. **1966**, 486. (c) M.D. Fryzuk, T.S. Haddad, and D.J. Berg, Coord. Chem. Rev. **1990**, 90, 137.

3. (a) L.F. Warren and M.A. Bennett, Inorg. Chem. **1976**, 15, 3126. (b) M.H. Jones, W. Levason, C.A. McAuliffe, and M.J. Parrott, J. Chem. Soc. Dalton Trans. **1976**, 1642.

4. R.L. Dentscher and D.L. Kepert, Inorg. Chem. **1970**, 9, 2305.

5. (a) J.L. Hoard and J.V. Silverton, Inorg. Chem. **1963**, 2, 235. (b) M.A. Porari-Koshits and L.A. Aslanov, J. Struct. Chem. **1972**, 13, 244. (c) E.L. Muetterties and L.J. Guggenberger, J. Am. Chem. Soc. **1974**, 96, 1748.

6. A. Zalkin, P.G. Edwards, D. Zhang, and R.A. Andersen, Acta Cryst. **1986**, C42, 1480.

7. D. Taylor and G.B. Robertson, private communication as quoted in footnote 36 of ref. 3a.

8. P. Bernstein, G.A. Rodley, R. Marsh, and H.B. Gray, Inorg. Chem. **1972**, 11, 3040.

9. P.G. Edwards, R.A. Andersen, and A. Zalkin, J. Am. Chem. Soc. **1981**, 103, 7792.

10. (a) G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett, and M.B. Hursthouse, J. Chem. Soc. Dalton Trans. **1985**, 1339. (b) J.M. Rosalky, Ph. D. thesis, Australian National University, 1975, quoted in footnote 53 of ref. 3a; the crystal structure of $MnCl_2(diphos)_2$ has been reported in abstract form: M.A.

Bennett, G.A. Robertson, J.M. Rosalky, L.F. Warren, Acta Cryst. **1975**, 31A, 5136.

11. G.N. LaMar, W. DeW. Horrocks, and R.H. Holm (eds.) "NMR of Paramagnetic Molecules" Academic Press, New York 1973.

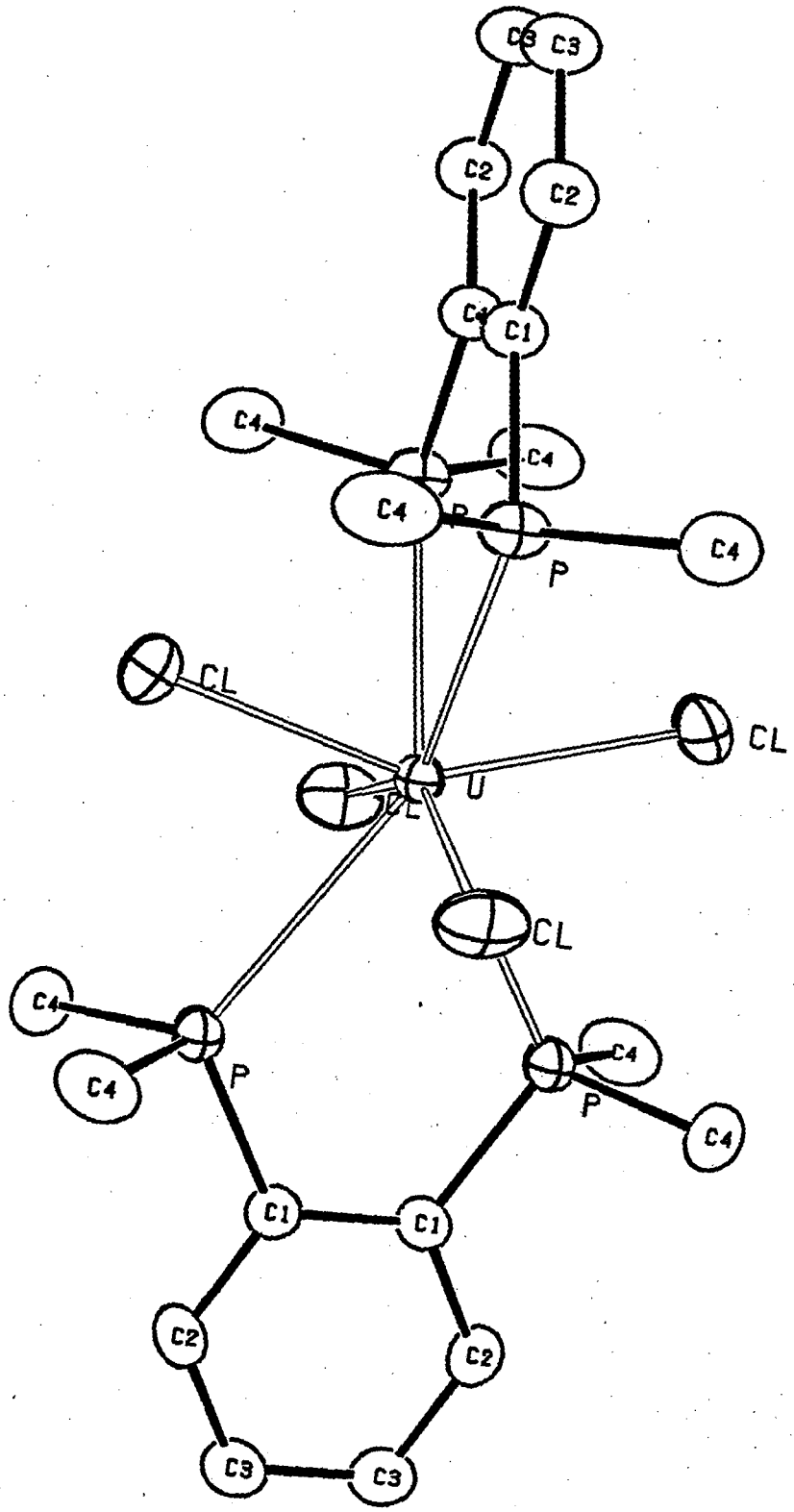
Table. Shape Parameters for UCl_4 (bidentate ligand)$_2$

Compound	δ'(deg)[a]	ϕ(deg)[a]
UCl_4(diphos)$_2$	26.1	0
UCl_4(diars)$_2$	24.1	0
D_{2d}-dodecahedron	29.5	0

[a]Defined in reference 5c.

Figure Caption

Figure 1. For $UCl_4(diphos)_2$, U-P = 2.981(1) Å, U-Cl = 2.627(1) Å, C-P (ave.) = 1.831(3) Å, C-C (ave.) = 1.391(4) Å, Cl-U-Cl = 148.61(5)° and 94.20(1)°, P-U-P = 134.53(2)° and 66.25(3)°. For $UCl_4(diars)_2$, U-As = 3.049(1) Å, U-Cl = 2.618(3) Å, As-C (ave.) = 1.945(2) Å, C-C (ave.) = 1.372(28) Å, Cl-U-Cl = 147.72(9)° and 94.43(9)°, As-U-As = 134.49(3)° and 66.32(3)°. The thermal ellipsoids represent 50% probability surfaces.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