Table 3 (cont.)

(c) Environment of water (1)

$O(W1)\cdots O(4^{ii})$	2·603 (7)	$O(W1)\cdots O(W2^v)$	3·255 (7)	
$O(W1)\cdots O(2^{iv})$	2·697 (7)	$O(4^{ii})\cdots O(W1)\cdots Fe$	97·2 (2)	
$O(W1)\cdots O(1^i)$	3·037 (7)	$O(2^{iv})\cdots O(W1)\cdots Fe$	128·8 (2)	
$O(W1)\cdots O(3^v)$	3·233 (7)	$O(4^{ii})\cdots O(W1)\cdots O(2^{iv})$	123·5 (2)	

(d) Environment of water (2)

$O(W2)\cdots O(3)$	2·643 (7)	$O(W2)\cdots O(1^{vi})$	3·264 (7)
$O(W2)\cdots O(4^i)$	3·130 (7)	$O(3)\cdots O(W2)\cdots Fe$	96·0 (2)
$O(W2)\cdots O(W1^{vi})$	3·255 (7)		

Symmetry operations

(i)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	(iv)	$\frac{1}{2}-x, \frac{1}{2}+y, z$	
(ii)	$\frac{1}{2}-x, -y, \frac{1}{2}+z$	(v)	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$	
(iii)	$1-x, -y, -z$	(vi)	$\frac{1}{2}+x, \frac{1}{2}-y, -z$	

molecules to OH_3^+ and OH^- has been suggested (Mooney-Slater, 1961). Such pseudo-water species, however, have not been found in metavariscite, $AlPO_4.2H_2O$; two types of water molecules are bound to the nearest phosphate oxygens with two normal and two bifurcated hydrogen bonds, respectively (Kniep & Mootz, 1973). Furthermore, in contrast to $InPO_4.2H_2O$, the distances of $Me-O(W1)$ are shorter than those of $Me-O(W2)$ for both scorodite and metavariscite. Thus, the bond nature of water in scorodite is more similar to that in metavariscite, in spite of the different space group, than to that in the isomorphous $InPO_4\ 2H_2O$.

The variation of hydrogen-bonding schemes in these homologous compounds seems to reflect the difference in size ratios of the cations to the anionic clusters and also in amphotericity of the trivalent cations.

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Tetrabromobis-[σ-phenylenebis(dimethylarsino)]tantalum(V) Hexabromotantalate(V)

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Abstract. $C_{20}H_{20}As_4Br_{10}Ta_2$, $M=1721·06$, tetragonal, $a=12·525$ (9), $c=25·474$ (23) Å, $U=3996·25$ Å^3, $Z=4$, $d_c=2·81$, $d_m=2·85$ (4), Cu $K\alpha$ radiation $\lambda=1·54178$ Å, μ(Cu $K\alpha$)$=272·97$ cm^{-1}. Space group $I4_1/amd$ from systematic absences $hkl, h+k+l=2n+1$; $hk0, h=2n+1$; $hhl, 2h+l\neq 4n$. This compound was prepared by Clark, Kepert & Nyholm [J. Chem. Soc. (1965), pp. 2877–2883] and formulated as $TaBr_5(diars)$, diars$=$ σ-phenylenebis(dimethylarsine). In fact the crystal structure determination shows it to be $[TaBr_4(diars)_2]^+$ $TaBr_6^-$. The cation is a crystallographically imposed dodecahedron [Ta–Br(1) 2·583 (10), Ta–As(1) 2·765 (1) Å] and the anion an octahedron [Ta–Br(1) 2·487 (12), Ta–Br(3) 2·490 (15) Å]. The 316 independent reflexions, measured by counter methods, have been refined to R 0·108.

Introduction. Crystals of $TaBr_5(diars)$ were prepared following the method of Clark, Kepert & Nyholm (1965) and recrystallized from dichloromethane by slow evaporation of the solvent. A crystal with dimensions $0·2 \times 0·15 \times 0·35$ mm was mounted with the a axis

parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Nickel-filtered copper X-radiation was used. 585 independent reflexions with $2\theta < 100°$ were measured by the stationary-crystal stationary-counter method. Several standard reflexions were measured repeatedly during the course of the experiment but no significant change of intensity was detected. The standard deviation $\sigma(I)$ of the reflexions was taken to be $[I + 2E + (0.03I^2)]^{1/2}$ where E is the estimated background of the reflexion. 316 reflexions with $I > \sigma(I)$ were used in subsequent calculations. An absorption correction was applied with the program *ABSORB* (Stewart, 1972). Maximum and minimum transmission factors were 0.40 and 0.12.

The structure was solved with considerable difficulty (as we were looking for vectors from a $TaBr_5$(diars) monomeric molecule) from the Patterson function and successive Fourier syntheses. The structure was refined by full-matrix least-squares calculations to R 0.108* with all atoms anisotropic except for the carbon atoms. All atoms except C(1) were in special positions, the Wyckoff notations of which are listed with the final positional coordinates in Table 1. Table 2 lists the final thermal parameters.†

The weighting scheme was chosen to give average values of $w\Delta^2$ for groups of reflexions independent of the values of F_o and $\sin \theta/\lambda$. It was $\sqrt{w} = 1$ for $F_o < 180$ and $\sqrt{w} = 180/F_o$, for $F_o > 180$. Calculations were made on a C.D.C. 7600 computer at the University of London Computer Centre using the X-RAY set of programs (Stewart, 1972). Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962) as were the corrections for the real and imaginary parts of the anomalous dispersion for the tantalum, bromine and arsenic atoms. The anisotropic temperature factors are defined as $\exp[-$

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* The high R value is due to the small size of the crystal and the large number of weak reflexions, only 156 having $I > 3\sigma(I)$.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30701 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positions* ($\times 10^4$) *with estimated standard deviations in parentheses*

Origin of space group $I4_1/amd$ (No. 141) at centre ($2/m$).
(a) Parameter fixed. (b) $y = x + \frac{1}{4}$.

	x	y	z	Wyckoff notation
Ta(1)	0000^a	2500^a	3750^a	b
Ta(2)	0000^a	2500^a	8750^a	a
Br(1)	0000^a	4631 (8)	4061 (4)	h
As(1)	0000^a	3842 (9)	2888 (4)	h
Br(2)	1404 (14)	3904^b	8750^a	g
Br(3)	0000^a	2500^a	9728 (6)	e
C(1)	1127 (68)	4874 (62)	2804 (32)	i
C(2)	0000^a	2990 (61)	2208 (31)	h
C(3)	0000^a	3678 (79)	1758 (36)	h
C(4)	0000^a	2907 (74)	1259 (36)	h

$0.25\pi^2 \sum_i \sum_j h_i h_j b_i b_j (i,j = 1\text{–}3)]$ where b_i is the ith reciprocal cell dimension. The 269 zero reflexions showed no large discrepancies. There were no extraneous peaks in a difference Fourier synthesis and in the final cycle of the refinement, all shifts were $< 0.15\sigma$. The dimensions of the cation and anion are given in Table 3.

Discussion. We have studied the structures of a number of seven-coordinate complexes of the early transition metals and have classified them according to the number of halogen atoms in the coordination sphere. Structures with one (Drew & Wilkins, 1974a), two (Drew & Wilkins, 1974b), three (Drew & Wilkins, 1974c) and four (Drew, Wilkins & Wolters, 1972) halogens (Cl, Br, I) are well established by X-ray crystallography and we therefore required a compound with five halogens to continue the series.

From the several complexes of MX_5L, X = halogen, L = a bidentate ligand, which have been reported as being seven-coordinate monomers, we chose $TaBr_5$-(diars) (Clark, Kepert & Nyholm, 1965) and have determined its crystal structure. However, the structure consists of discrete ions $[TaBr_4(diars)_2]^+$, $TaBr_6^-$, and not the monomeric structure that was suggested by Clark *et al.* (1965). They measured the conductivities of the complexes MX_5(diars), X = Br, Cl in several solvents and found that the solutions had significant conductivities which were however rather low for 1:1 electrolytes (Geary, 1971). They attributed this conductivity to slight hydrolysis of the complexes in solution and concluded that the structures were non-ionic

Table 2. *Thermal parameters* ($\times 10^3$) *with estimated standard deviations in parentheses*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	70.9 (39)	70.9^b	51.1 (49)	00^a	00^a	00^a
Ta(2)	85.2 (45)	85.2^b	63.7 (55)	00^a	00^a	00^a
Br(1)	121 (9)	59 (6)	74 (6)	00^a	00^a	−09 (5)
As(1)	76 (7)	95 (8)	62 (6)	00^a	00^a	09 (6)
Br(2)	114 (11)	114^b	112 (7)	−09 (7)	−11 (11)	11^c
Br(3)	132 (15)	180 (20)	63 (8)	00^a	00^a	00^a

(a) Parameter fixed. (b) $U_{22} = U_{11}$. (c) $U_{23} = -U_{13}$.

Isotropic thermal parameters are defined as $\exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$. Values of U ($\times 10^3$) are C(1) 136 (29), C(2) 87 (31), C(3) 96 (29), C(4) 113 (37).

Table 3. *Bond lengths* (Å) *and angles* (°)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference atoms (in Table 1) at x,y,z.

(i) $x,\frac{1}{2}-y,z$; (ii) $\frac{1}{4}-y,\frac{1}{2}-x,\frac{3}{4}-z$; (iii) $-x,y,z$.

Ta(1)–Br(1)	2·583 (10)	Ta(2)–Br(2)	2·487 (12)
Ta(1)–As(1)	2·765 (10)	Ta(2)–Br(3)	2·490 (15)
As(1)–Ta(1)–As(1ᴵ)	74·9 (3)	As(1)–C(1)	1·92 (8)
As(1)–Ta(1)–As(1ᴵᴵ)	129·1 (2)	As(1)–C(2)	2·03 (8)
As(1)–Ta(1)–Br(1)	70·4 (3)	C(2)—C(2ᴵ)	1·23 (11)
As(1)–Ta(1)–Br(1ᴵ)	145·3 (3)	C(2)—C(3)	1·43 (12)
As(1)–Ta(1)–Br(1ᴵᴵ)	75·9 (2)	C(3)—C(4)	1·60 (13)
Br(1)–Ta(1)–Br(1ᴵ)	144·3 (3)	C(4)—C(4ᴵ)	1·02 (14)
Br(1)–Ta(1)–Br(1ᴵᴵ)	95·4 (1)		
Ta(1)–As(1)–C(1)	119·7 (25)	As(1)–C(2)–C(2ᴵ)	122 (6)
Ta(1)–As(1)–C(2)	110·9 (22)	C(2ᴵ)–C(2)–C(3)	127 (8)
C(1)—As(1)–C(2)	118·0 (26)	C(2)—C(3)–C(4)	106 (7)
C(1)—As(1)–C(1ᴵᴵᴵ)	94·3 (34)	C(3)—C(4)–C(4ᴵ)	127 (10)
As(1)–C(2)—C(3)	111 (6)		

monomers. Knowing now that the solutions contain ions, we conclude that the conductivities were less than expected because of the large size of the ions.

The discrete ions have the expected geometries. In the cation the metal atom has crystallographically imposed dodecahedral symmetry as has been found in TiCl$_4$(diars)$_2$ by Clark, Lewis, Nyholm, Pauling & Robertson (1961) and in [MoCl$_4$(diars)$_2$]$^+$ by Drew, Egginton & Wilkins (1974). The anion is an octahedron.

So why is TaBr$_5$(diars) not a seven-coordinate monomer? We have demonstrated previously (Drew & Wilkins, 1974c) that X···X repulsions in the coordination sphere are one of the most important factors in determining the molecular geometry of high coordinate monomers. Indeed in the majority* of such compounds X–M–X angles are $\geq 90°$. This is clearly impossible for five halogens in a seven-coordinate monomer while easily satisfied in a MX$_4$(diars)$_2$ dodecahedron where X–M–X angles are *ca* 95°. Also in favour of the ionic

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* In only one compound are angles of this type much less than 90°. This is WOCl$_4$(diars) (Drew & Mandyczewsky, 1970) which is a pentagonal bipyramid with three chlorines and diars in the equatorial girdle. Presumably in this molecule the multiply bonded oxygen atom takes precedence over chlorine in occupying an axial site. Cl–W–Cl angles are *ca* 76°.

structure is that the diars ligand is well suited to the dodecahedron (Drew, Egginton & Wilkins, 1974).

Our present results suggest that other compounds formulated as MX$_5$L may not be seven-coordinate monomers.*

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* TaCl$_5$(diars) has been established as ionic from a crystal structure determination (Drew & Wilkins, 1974d). Thus NbCl$_5$(diars) and WCl$_5$(diars) which are isomorphous (Blight, Kepert, Mandyczewsky & Trigwell, 1972) are also ionic. This contrasts with WOCl$_4$(diars) which is monomeric presumably because of the stabilizing effect of the multiple bond.

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