Preparation of New Vanadium(II) Iodides and Crystal Structure of Hexakis(acetonitrile)vanadium(II) (Tetraiodide)†

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The reaction of $[VCl_3(MeCN)_3]$ with $SiMe_3I$ in acetonitrile under reflux yielded a vanadium(II) cation $[V(MeCN)_6]^{2+}$ with a counter ion I_4^{2-}. The latter is not symmetrical, though linear, and the reasons are discussed. The new compound diiodotetrakis(tetrahydrofuran)vanadium(II) is shown to be a versatile precursor for vanadium diiodides, such as $[VI_2(Et_2PCH_2CH_2PEt_2)_2]$, the structure of which has also been determined.

We have recently described[1] the ultimately successful synthesis of $[VI_2(salen)]$ [H_2salen = *N,N'*-ethylenebis(salicylideneimine)], a complex with an expected octahedral structure with *trans* iodides. We had found that reactions expected to yield this complex, such as [VO(salen)] with I_2[2] or HI[3] actually caused oxidation or reduction, yielding $[V^{IV}O(salen)V^{V}O(salen)]^+$ and $[\{V^{IV}(salen)OV^{III}(salen)\}_2]^{2+}$, respectively. Our successful procedure involved [VO(salen)] and $SiMe_3I$.

This reaction suggested that dry $SiMe_3I$ might well be a general reagent for making iodides, avoiding redox reactions. We discovered that this actually can be the case, but that there seems to be no general metathetical route to vanadium iodides. Here we describe the results of a range of reactions which allow the synthesis of vanadium(II) iodides.

Results and Discussion

We first attempted to obtain a vanadium(III) iodide by a simple halide-exchange reaction involving $[VCl_3(MeCN)_3]$[4] and $SiMe_3I$ in MeCN at reflux. Vanadium(III) iodide[5] itself is known, but not easily accessible or very stable. The analysis of our product could not be rationalised, though it clearly contained V^{II}, but the structure was determined unequivocally by X-ray analysis. Atomic coordinates and bond lengths and angles are given in Tables 1 and 2, and a representation of the structure is shown in Fig. 1.

The salt (Λ_M = 405 ohm^{-1} cm^2 mol^{-1}, 10^{-3} mol dm^{-3}, MeCN) product contains vanadium(II) cations, $[V(MeCN)_6]^{2+}$, and anions which are designated as I_4^{2-}. The magnetic moment is 3.66 μ_B (*ca.* 34 × 10^{-24} J T^{-1}), slightly low for V^{II}. The co-ordination about the vanadium is, as might be expected, regular, octahedral, with the acetonitrile co-ordinated linearly and end-on. However, though the acetonitrile nitrogen atoms are apparently precisely co-ordinated in regular octahedral positions, and the N–V–N angles are within 3° of the ideal 90 or 180° (with one exception), the departures from the ideals do appear to have some significance. This will be discussed below, along with the detailed structure of the I_4^{2-} ion. The V–NCMe bond lengths are all very similar and normal.[6]

The first surprise in the structure is the presence of vanadium(II), generated under very mild conditions. The reductant appears to be covalent or ionic iodide. The latter could be generated by traces of moisture from $SiMe_3I$, but we do not know if this happens. The ultimate silicon-containing product was not identified. We know that HI can reduce V^{IV} to V^{III},[3] but it was not known that reduction further to V^{II} might also be possible. However, consistent with the presence of water-generated iodide, the oxidised redox partner appears to be a species we write as I_4^{2-}, formally comprised of $I_2 + 2I^-$, or even $I_3^- + I^-$. The structure of this material is now discussed.

Table 1 Final atomic coordinates (fractional × 10^4) for $[V(NCMe)_6][I_4]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	2500	1625(1)	5000
N(1)	1477(8)	926(5)	4029(9)
C(1)	912(9)	558(5)	3566(10)
C(11)	175(13)	56(7)	2990(13)
N(2)	3908(8)	1626(4)	3600(9)
C(2)	4632(11)	1631(5)	2905(13)
C(21)	5664(11)	1658(6)	1925(12)
N(3)	3436(8)	2344(5)	5956(8)
C(3)	3844(10)	2767(6)	6399(11)
C(31)	4373(12)	3334(6)	6959(14)
I(1)	2500	7376.2(7)	5000
I(2)	2500	6070.2(6)	5000
I(3)	2500	4617.1(6)	5000
I(4)	2500	8989.9(5)	5000

The four-iodine unit is strictly linear, but the separations are not symmetrical, being 3.166(2), 2.846(2) and 3.516(2) Å in order along the chain. The terminal iodine atoms are at different distances from their nearest vanadium neighbours, 6.520(3) and 5.741(3) Å, respectively, so that V–I bonding can be excluded. Apparently we have an isolated group of four iodine atoms, arranged in a strict line, but it is not at first sight obvious whether they should be regarded more as $I^- + I_3^-$ rather than I_4^{2-}.

There have been several discussions of the structures of polyhalide, including polyiodide, ions. For an isolated I_4^{2-} ion, a linear symmetrical structure has been calculated,[7] with a central bond length of 2.807 Å and two relatively long peripheral bonds of 3.991 Å. This is apparently best regarded as $I_2 + 2I^-$.[8] The single bond in I_2 has a length of 2.677 Å in the gas phase and 2.715 Å in the solid state.[7] According to Wiebenga and Kracht,[9] breakdown in maximum symmetry for polyhalide ions is a function of the field in which the polyhalide

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 2 Molecular dimensions in [$V(NCMe)_6$][I_4]; bond lengths in Å, angles in °. E.s.d.s are given in parentheses

(*a*) About the vanadium atom			
V-N(1)	2.128(10)	V-N(3)	2.108(10)
V-N(2)	2.111(10)		
N(1)-V-N(1′)	88.7(4)	N(2)-V-N(2′)	179.9(4)
N(1)-V-N(2)	91.6(4)	N(2)-V-N(3)	89.9(3)
N(1)-V-N(2′)	88.5(4)	N(2)-V-N(3′)	90.0(3)
N(1)-V-N(3)	177.3(3)	N(3)-V-N(3′)	84.0(4)
N(1)-V-N(3′)	93.7(4)		
(*b*) In the acetonitrile ligands			
N(1)-C(1)	1.113(14)	V-N(1)-C(1)	177.0(9)
C(1)-C(11)	1.474(17)	N(1)-C(1)-C(11)	178.0(13)
N(2)-C(2)	1.068(15)	V-N(2)-C(2)	178.9(10)
C(2)-C(21)	1.514(17)	N(2)-C(2)-C(21)	178.3(13)
N(3)-C(3)	1.119(14)	V-N(3)-C(3)	172.5(9)
C(3)-C(31)	1.480(17)	N(3)-C(3)-C(31)	178.7(13)
(*c*) In the anion			
I(1)-I(2)	2.846(2)	I(2)-I(1)-I(4)	180.0
I(2)-I(3)	3.166(2)	I(1)-I(2)-I(3)	180.0
I(1)-I(4)	3.516(2)		

Primed atoms are at 0.5 − *x*, *y*, 1 − *z*.

finds itself, so that is presumably where we must seek the reason for the asymmetry of our polyiodide. These authors[9] also derived a bond-order/bond-length relationship. This produces estimated bond orders in our polyiodide of about 0.50, 0.75 and 0.33. This effectively excludes a formulation $I^- + I_3^-$.

The ion I_4^{2-} has been recognised in several different structural situations. Generally there are clear covalent links of some kind, as in $Cu(NH_3)_4I_4$, with a Cu–I–I–I–I–Cu system bent almost to 90° at each terminal I, linear iodine arrangement, and I–I separations of 3.342(1) (peripheral) and 2.802(1) (central) Å.[10] In [$\{Ir(C_5Me_5)\}_2I_6$][11] and some platinum complexes[12] the arrangement is rather similar, though the angles of 90° open to more than 100° and may reach 126°. There is no necessary centre of symmetry, the central I–I separation is between 2.75 and 2.79 Å, and the peripheral separations vary from 3.24 to 3.56 Å. The platinum complexes are discussed in terms of I_2 molecules bridging between iodide co-ordinated to two different platinum atoms.

However, co-ordination is not necessary to stabilise I_4 groups. Thus in [$\{UO_2(OH)[CO(NH_2)_2]_3\}_2$]$I_4$ there is a linear symmetrical I_4 with I–I separations of 3.40 (peripheral) and 2.70 (internal) Å, and hydrogen bonding to all the iodine atoms.[13] Tetrakis(4′-ethoxyacetanilide) dihydrogentetraiodide dihydrate contains linear symmetrical I_4^{2-} strongly hydrogen bonded [I–I 3.404(1) and 2.774(1) Å] into a chain by water molecules.[14] The adducts ethylenethiourea–diiodine (1/2) and ethylenethiourea–diiodine (1/3) apparently contain neutral I_4.[15] However, the unit is bent at 90° at one of the inner iodines and there are strong I–S interactions.

The only apparent example of an I_4^{2-} unit completely free of covalent interactions with other atoms is in Tl_6PbI_{10}, and in this case the system is linear and symmetrical, with I–I separations of 3.11–3.18 Å.[16] This is not close to the theoretical prediction.[8] Why is our case, also without obvious covalent interactions, so very different?

From Fig. 1 we note that the iodine closer to vanadium, I(4), is the ‘isolated’ member of the chain. To accommodate it, the acetonitrile molecules closest to it are bent slightly outwards, without significantly affecting the co-ordination sphere of the vanadium. Conceivably there are minor I–H–C interactions. Its iodine neighbour I(1) has no such interactions, but I(2) does seem to interact with further co-ordinated acetonitriles in the *bc* plane. Finally I(3), the further of the two terminal iodine atoms from vanadium, still seems to interact because the methyl groups of co-ordinated acetonitrile are pulled towards it by bending slightly inwards.

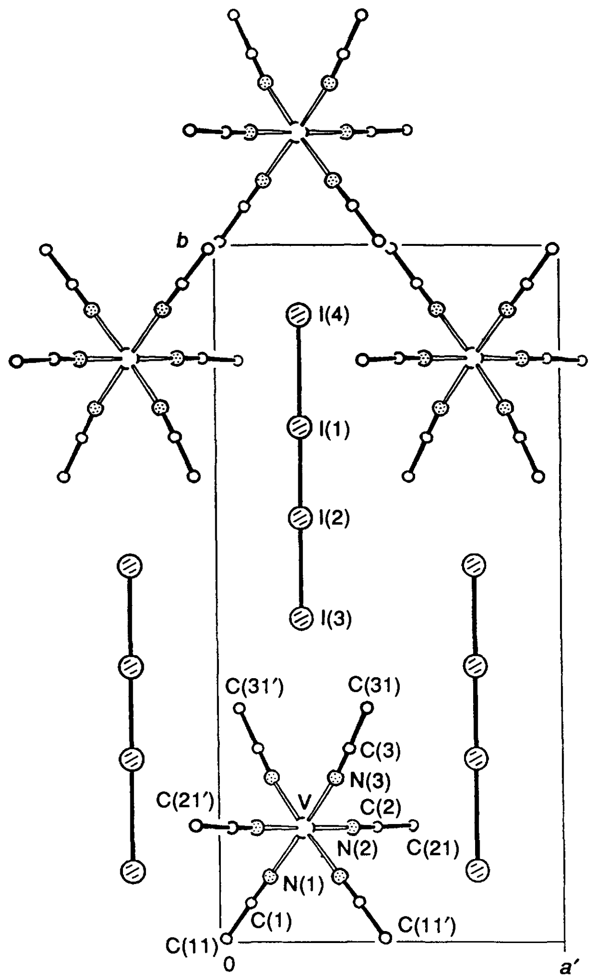
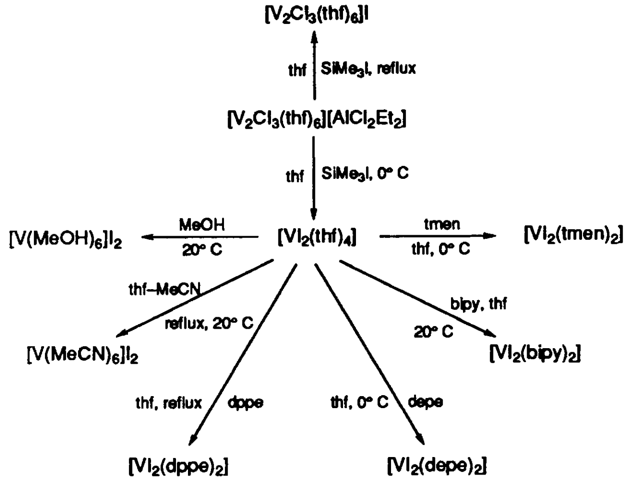


Fig. 1 Structure of [$V(MeCN)_6$][I_4] viewed down the *c* axis. Atoms whose coordinates are in Table 1 are labelled; atoms with primed numbers are related to these by a two-fold symmetry axis

We cannot explain why this asymmetry arises. However, it does seem clear that we do indeed have a form of I_4^{2-}, that there are several non-bonding interactions contributing to the final structure, and that the polyiodide is very easily deformable. The data suggest many interesting experimental extrapolations.

For preparations of vanadium(II) iodides, a key intermediate was found to be [$VI_2(thf)_4$] (thf = tetrahydrofuran). This may be *cis*, by analogy with the known [$VI_2(MeOCH_2CH_2OMe)_2$][17] and was prepared from the well established dinuclear cation [$V_2Cl_3(thf)_6$]$^+$ by reaction of the [$AlCl_2Et_2$]$^-$ salt[18] with $SiMe_3I$ in thf at 0 °C. If the same reactants are heated under reflux for 2 h, then the product ultimately crystallising is the known[17] [$V_2Cl_3(thf)_6$]I. This apparently surprising result may be a reflection of the fact that, in vanadium(II) chemistry, polynuclear species are favoured by higher temperatures. Another example is the relative stabilities of [$V_3Cl_5(tmen)$]$^+$ and [$VCl_2(tmen)_2$] (tmen = *N,N,N′,N′*-tetramethylethylenediamine), for which the trinuclear species is the more stable at the higher temperature.[19] The various transformations are shown in Scheme 1. Both MeCN and MeOH seem to be able to displace all the other ligands, including iodide, to yield hexa(ligand) species (ligand = MeCN or MeOH). The chloro analogues of the phosphine complexes



Scheme 1 Routes to vanadium(II) iodides

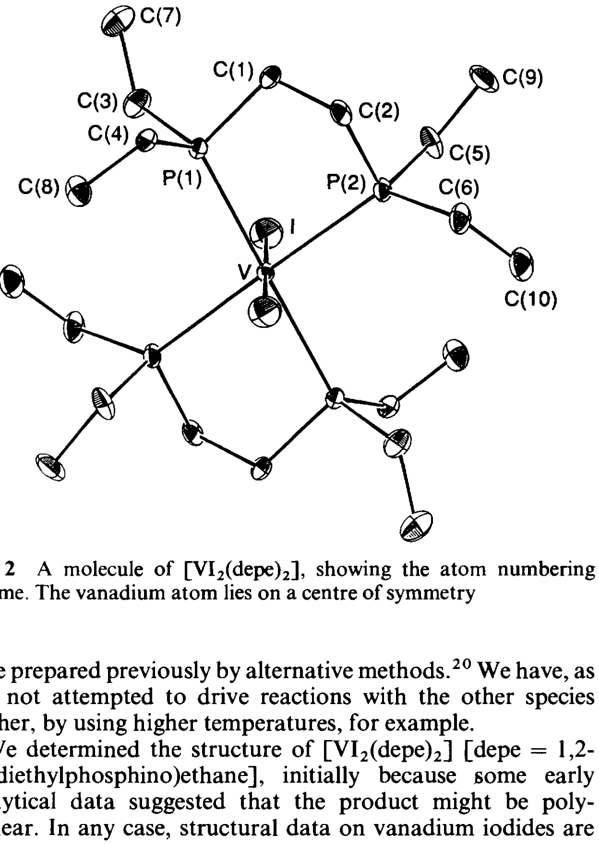


Fig. 2 A molecule of $[VI_2(depe)_2]$, showing the atom numbering scheme. The vanadium atom lies on a centre of symmetry

were prepared previously by alternative methods.[20] We have, as yet, not attempted to drive reactions with the other species further, by using higher temperatures, for example.

We determined the structure of $[VI_2(depe)_2]$ [depe = 1,2-bis(diethylphosphino)ethane], initially because some early analytical data suggested that the product might be polynuclear. In any case, structural data on vanadium iodides are scarce. A representation of the structure is shown in Fig. 2, and atomic coordinates and bond lengths and angles are given in Tables 3 and 4.

The structure of $[VI_2(depe)_2]$ is regular, *trans*, octahedral. There is nothing unusual about it. However, minor comments on the bond lengths are in order. The V–I bond length is 2.779(1) Å. There are six other reports of V–I bond lengths in the literature. Three of vanadium(IV) compounds span the range of 2.5441(1)–2.653(2) Å.[21] Our own determination of $[VI_2(salen)]$ was unexpectedly long at *ca.* 2.76 Å.[1] A vanadium(III) determination yielded a value of 2.794(1) Å,[22] and the single other vanadium(II) value in $[VI_2(MeOCH_2CH_2OMe)_2]$ gave 2.808(2) Å.[17] Our new bond length is towards the longer end of the range. We conclude that there is a rough correlation between V–I bond lengths and vanadium oxidation state, but there is only a relatively small range available as yet. There are few determinations of V–P bond lengths. Our two values are very similar, at 2.562(3) and 2.572(3) Å. In $[VCl_3(PMePh_2)_3]$ and $[VCl_3(MeCN)(PMePh_2)_2]$ values of 2.53 and 2.55 Å have been reported,[20a] whereas in the vanadium(II) species $[VCl_2(dmpe)_2]$ [dmpe = 1,2-bis(dimethylphosphino)ethane],[20b] $[VCl_2(depe)_2]$ and $[VCl_2(dppe)_2]\cdot 2thf$ [dppe = 1,2-bis(diphenylphosphino)ethane] the V–P distances are *ca.* 2.50, 2.56 and 2.56 Å.[23] Even in V^V species the distances turn out to be *ca.* 2.53 Å.[24] Clearly the V–P separations are not very elastic. This is in contrast to the situation in iron phosphine complexes, in which the iron–halogen bonds are relatively invariant but the iron–phosphorus bonds appear to be very soft.[25]

Table 3 Final atomic coordinates (fractional × 10^4) for $[VI_2(depe)_2]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
V	0	0	0
I	2260.6(10)	−2065.2(9)	−168.8(9)
P(1)	1534(3)	1445(3)	−1464(3)
P(2)	1993(3)	2471(3)	1738(3)
C(1)	3184(15)	3153(13)	−416(11)
C(2)	2600(14)	3960(12)	870(11)
C(3)	2648(14)	319(12)	−2665(11)
C(4)	435(13)	2593(11)	−2327(10)
C(5)	3998(14)	2154(12)	2407(11)
C(6)	1361(15)	3840(12)	3175(11)
C(7)	3947(16)	1320(14)	−3199(12)
C(8)	−1054(15)	1533(12)	−3345(11)
C(9)	5343(15)	3673(13)	3147(12)
C(10)	1290(17)	3230(13)	4333(12)

Table 4 Molecular dimensions in $[VI_2(depe)_2]$; bond lengths in Å, angles in °. E.s.d.s are given in parentheses

(*a*) About the vanadium atom

V–I	2.779(1)	I–V–P(1)	90.02(6)
V–P(1)	2.572(3)	I–V–P(2)	94.08(6)
V–P(2)	2.562(3)	P(1)–V–P(2)	79.54(9)

(*b*) In the depe ligand

P(1)–C(1)	1.816(12)	C(1)–C(2)	1.53(2)
P(1)–C(3)	1.819(11)	C(3)–C(7)	1.52(2)
P(1)–C(4)	1.829(11)	C(4)–C(8)	1.51(2)
P(2)–C(2)	1.824(12)	C(5)–C(9)	1.51(2)
P(2)–C(5)	1.832(11)	C(6)–C(10)	1.49(2)
P(2)–C(6)	1.846(11)		
V–P(1)–C(1)	108.0(4)	C(2)–P(2)–C(5)	103.5(6)
V–P(1)–C(3)	120.4(4)	C(2)–P(2)–C(6)	100.0(5)
V–P(1)–C(4)	119.3(4)	C(5)–P(2)–C(6)	103.2(5)
C(1)–P(1)–C(3)	102.6(6)	P(1)–C(1)–C(2)	110.0(8)
C(1)–P(1)–C(4)	99.3(5)	P(2)–C(2)–C(1)	112.1(7)
C(3)–P(1)–C(4)	104.2(5)	P(1)–C(3)–C(7)	118.1(8)
V–P(2)–C(2)	104.2(4)	P(1)–C(4)–C(8)	114.7(7)
V–P(2)–C(5)	118.1(4)	P(2)–C(5)–C(9)	117.9(8)
V–P(2)–C(6)	124.5(4)	P(2)–C(6)–C(10)	116.1(8)

Experimental

Preparations were carried out using standard Schlenk techniques, under pure, dry N_2. Acetonitrile was dried by distillation from calcium hydride, and tetrahydrofuran was dried by distillation from sodium–benzophenone. The compounds $[VCl_3(thf)_3]$[26] and $[VCl_3(MeCN)_3]$[4] were obtained by heating VCl_3 overnight in solvent under reflux, filtering, cooling, and allowing the required materials to crystallise. The salt $[V_2Cl_3(thf)_6][AlCl_2Et_2]$[18] was prepared by a literature method. Diphosphines were prepared as described earlier,[27] and all other materials were obtained commercially. Microanalyses (C, H and N) were by the University of Surrey Microanalytical Service, Cl and I by Butterworth Analytical Laboratories. Conductivities were obtained using a Portland

Electronics bridge, and magnetic moments were determined at ambient temperature by the Faraday method using Hg[Co(NCS)$_4$] as standard.

Preparation.—Diiodotetrakis(tetrahydrofuran)vanadium(II). Iodotrimethylsilane (8.0 cm^3, 11.2 g, 56 mmol) was added in one portion to a stirred solution of [V$_2$Cl$_3$(thf)$_6$][AlCl$_2$Et$_2$] (4.0 g, 5.0 mmol) in thf (24 cm^3) at 0 °C. A light-green precipitate formed after *ca.* 10 s. After 30 min at -20 °C, the precipitate was filtered off, washed with thf (4 × 2 cm^3) and diethyl ether (4 × 4 cm^3) and dried *in vacuo*. Yield 4.3 g, 72% (Found: C, 32.2; H, 5.5; Cl, < 0.2. $C_{16}H_{32}I_2O_4V$ requires C, 32.4; H, 5.5; Cl, 0.0%).

Trichlorohexakis(tetrahydrofuran)divanadium(II) *iodide*. When the reactants as above were heated under reflux for 2 h, a clear green solution was obtained. On cooling this to -20 °C overnight, the known [V$_2$Cl$_3$(thf)$_6$]I (2.04 g, 53%) crystallised (Found: C, 37.7; H, 6.5; Cl, 13.9. $C_{24}H_{48}Cl_3IO_6V_2$ requires C, 37.5; H, 6.3; Cl, 13.8%).

The addition of SiMe$_3$I (4 cm^3) to the filtrate from the above preparation at 0 °C yielded [VI$_2$(thf)$_4$] (1.37 g, 23%).

Hexakis(methanol)vanadium(II) *diiodide*. To [VI$_2$(thf)$_4$] (2.2 g, 3.7 cm^3) was added MeOH (10 cm^3), giving a purple solution. The solvent was reduced *in vacuo*, and the residue was shaken with diethyl ether, giving a purple powder (1.65 g, 90%). This was recrystallised by dissolving in MeOH (1 cm^3) and layering with diethyl ether (Found: C, 14.3; H, 5.0. $C_6H_{24}I_2O_6V$ requires C, 14.5; H, 4.9%).

Hexakis(acetonitrile)vanadium(II) *diiodide*. To [VI$_2$(thf)$_4$] (1.0 g, 1.68 mmol) in thf (40 cm^3), MeCN (10 cm^3) was added. Blue crystals separated. These were filtered off, dissolved in MeCN (10 cm^3), and crystallisation caused by adding diethyl ether (40 cm^3). Yield 0.60 g, 65% (Found: C, 25.9; H, 3.2; N, 14.8. $C_{12}H_{18}I_2N_6V$ requires C, 26.2; H, 3.3; N, 15.2%).

Bis[1,2-*bis(diphenylphosphino)ethane*]*diiodovanadium*(II). 1,2-Bis(diphenylphosphino)ethane (2.4 g, 6.0 mmol) was added to a solution of [VI$_2$(thf)$_4$] (1.77 g, 3.0 mmol) in thf (100 cm^3) at reflux. The light green solution turned dark green. The solution was cooled to 20 °C, and toluene (100 cm^3) added. The volume was reduced *in vacuo* until a light-green powder precipitated. This was filtered off, and washed with thf–toluene (1:4) and diethyl ether. Yield 1.2 g, 37% (Found: C, 56.5; H, 4.3. $C_{52}H_{48}I_2P_4V$ requires C, 56.7; H, 4.4%).

Bis[1,2-*bis(diethylphosphino)ethane*]*diiodovanadium*(II). 1,2-Bis(diethylphosphino)ethane (5.0 cm^3, 20 mmol) was added to [VI$_2$(thf)$_4$] (1.18 g, 2.0 mmol) in thf (20 cm^3) at 0 °C. A green precipitate resulted, which gradually turned light blue. This was recrystallised from thf as blue crystals. Yield 0.90 g, 63% (Found: C, 33.9; H, 7.1. $C_{20}H_{48}I_2P_4V$ requires C, 33.5; H, 6.7%).

Bis(2,2′-bipyridine)diiodovanadium(II). To thf (30 cm^3) was added [VI$_2$(thf)$_4$] (0.75 g, 1.26 mmol) and 2,2′-bipyridine (bipy) (0.94 g, 6.3 mmol). A dark green crystalline precipitate formed immediately. This was filtered off and washed with copious amounts of thf and diethyl ether. Yield 0.62 g, 80% (Found: C, 38.6; H, 2.7; N, 8.4. $C_{20}H_{16}I_2N_4V$ requires C, 38.9; H, 2.6; N, 9.1%).

Diiodobis(N,N,N′,N′-*tetramethylethylenediamine*)*vanadium*(II). *N,N,N′,N′*-Tetramethylethylenediamine (4.0 cm^3, 3.1 g, 28 mmol) was added to [VI$_2$(thf)$_4$] (1.18 g, 2.0 mmol) in thf (40 cm^3) at 0 °C. The resultant blue solution deposited a blue powder when the volume was reduced *in vacuo* to 10 cm^3 at 0 °C. This was filtered off and washed with diethyl ether. Yield 0.50 g, 46% (Found: C, 26.7; H, 6.3; N, 10.4. $C_{12}H_{32}I_2N_4V$ requires C, 26.8; H, 6.0; N, 10.4%). If the reaction mixture was held at -20 °C, [VI$_2$(tmen)$_2$] separated as turquoise crystals.

Hexakis(acetonitrile)vanadium(II) (*tetraiodide*). A solution of [VCl$_3$(MeCN)$_3$] (2.8 g, 10.0 mmol) in acetonitrile (100 cm^3) was heated to reflux and SiMe$_3$I (8.0 cm^3, 56 mmol) was added, giving a dark blue solution. The acetonitrile was distilled out during 2 h, until the volume had been reduced to 40 cm^3. The remaining solution was cooled to 20 °C and dark blue crystals (4.0 g, 50%) were filtered off and washed with cold acetonitrile and diethyl ether (Found: C, 17.8; H, 2.2; N, 10.2. $C_{12}H_{18}I_4N_6V$ requires C, 17.9; H, 2.3; N, 10.4%).

The crystal used in the structure analysis was obtained by further recrystallisation from acetonitrile.

Crystal-structure Analysis of [V(MeCN)$_6$][I$_4$].—*Crystal data.* $C_{12}H_{18}I_4N_6V$, $M = 804.9$, monoclinic, space group $A2/a$ (equivalent to no. 15), $a = 10.638(1)$, $b = 21.788(3)$, $c = 10.538(1)$ Å, $\beta = 90.497(8)°$, $U = 2442.3$ Å^3, $Z = 4$, $D_c = 2.189$ g cm^{-3}, $F(000) = 1468$, μ(Mo-Kα) = 54.1 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å, $T = 293$ K.

The crystals are air-sensitive, very dark brown, diamond-shaped plates of varying thickness, with striations parallel to a plate edge. One crystal, *ca.* 0.17 × 0.33 × 0.77 mm, was sealed in a glass capillary and, after photographic examination, transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (by refinement from the settings of 25 reflections, $10 < \theta < 12°$, each reflection centred in four orientations) and for measurement of diffraction intensities (to θ_{max} 23°).

After correction for Lorentz–polarisation effects, crystal deterioration (uniform and steady, *ca.* 47% overall) and absorption (by semi-empirical ψ-scan methods), and adjusting for negative net values (by Bayesian statistical methods), the 1709 unique diffraction intensities were input to the SHELX system of programs.[28] Here, a rough molecular structure was determined from the automated Patterson routines (PATT) of SHELXS,[29] and the crystal structure, with an asymmetric displacement of the four I atoms along a two-fold symmetry axis, was achieved by a trial-and-error shifting of the basic molecular unit along the *b* axis.

Refinement, by full-matrix least-squares methods, with all atoms allowed anisotropic thermal parameters (no hydrogen atoms were included), converged with $R = 0.065$ and R'[28] = 0.077 for 1529 reflections ($I \geqslant \sigma_I$) weighted $w = (\sigma_F^2 + 0.0296\,F^2)^{-1}$. In a final difference map, the highest peaks, *ca.* 3 e Å^{-3}, were all along the two-fold symmetry axes.

Scattering factor curves for neutral atoms were taken from ref. 30. Computer programs used in this analysis have been noted above and in Table 4 of ref. 31, and were run on the DEC MicroVAX 3600 machine in the NFL.

Crystal-structure Analysis of trans-[VI$_2$(depe)$_2$].—*Crystal data.* $C_{20}H_{48}I_2P_4V$, $M = 717.3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.229(6)$, $b = 8.598(6)$, $c = 10.825(11)$ Å, $\alpha = 106.69(7)$, $\beta = 95.82(7)$, $\gamma = 100.39(6)°$, $U = 712$ Å^3, $Z = 1$, $D_c = 1.67$ g cm^{-3}, $F(000) = 357$, μ(Mo-Kα) = 27 cm^{-1}, $T = 173$ K.

The crystals are purple plate-like needles, striated lengthwise; one, cut to 0.3 × 0.2 × 0.10 mm, was mounted on a glass fibre on an Enraf-Nonius CAD4 diffractometer. Cell parameters were determined and intensity data (to θ_{max} 25°) measured in similar procedures to those described above.

The diffraction intensities were corrected for Lorentz–polarisation effects; no deterioration correction was necessary; an absorption correction was applied using DIFABS.[32] A total of 2499 unique reflections were recorded, 2071 of which had $I > 2\sigma_I$.

The structure was determined by the heavy-atom methods in SHELXS,[29] and refinement was by full-matrix least-squares methods in the Enraf–Nonius MolEN programs.[33] All the non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included in fixed, calculated positions with isotropic thermal parameters U_{iso} set at 1.3 U_{eq} for the parent C atom. At convergence, R and R' were 0.073 and 0.084 for the 2071 observed data weighted $w = \sigma_F^{-2}$. The highest peaks in the final difference map were *ca.* 1.65 e Å^{-3}, near the I atom.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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