

## 2-(Diphenylphosphinoyl)propanoate complexes: crystal structure of tris[2-(diphenylphosphinoyl)propanoato]vanadium(III)

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2-(Diphenylphosphinoyl)propanoic acid (Hdpop) has been prepared by a simple one-step procedure. The anion behaves as a versatile bidentate ligand, which co-ordinates to cations of  $V^{III}$ ,  $Cr^{III}$  and  $Fe^{III}$  to give octahedral tris(chelate) complexes of the type  $M(dpop)_3$ , to  $Sn^{IV}$  to give  $SnR_3(dpop)$  and  $SnR_2(dpop)_2$  ( $R = Me$  or  $Ph$ ), and to  $Mo^{VI}$  to give *cis*-[ $MoO_2(dpop)_2$ ]. The derivative  $Tl(dpop)$ , on the other hand, appears to be co-ordinated through the carboxylate group only. The  $\alpha$ -hydrogen of the  $dpop$  ligands of the molybdenum and thallium complexes undergo a slow and reversible hydrogen–deuterium exchange reaction with deuterio-methanol, and the mechanism of this process is discussed. The structure of  $V(dpop)_3 \cdot H_2O \cdot CH_2Cl_2$ , a rare example of a tris(dioxygen) chelate complex of vanadium(III), has been determined by single-crystal X-ray methods. There are two pairs of optical antipodes,  $\Lambda(R,R,R)$  and  $\Delta(S,S,S)$ , in the unit cell. The arrangement of donors about the metal is facial, with all the six-membered chelate rings adopting boat conformations. All the O–V–O bond angles are close to  $90^\circ$ , and the V–O(P) bond lengths averaging 2.023(2) Å are slightly longer than those of V–O(C) at 1.979(2) Å.

The co-ordination chemistry of the phosphoryl (P=O) donor has been extensively studied for many years. The bulk of the published work has been concerned with simple unidentate ligands such as the useful polar solvent hexamethylphosphoramide,  $P(NMe_2)_3O$ , and the actinide extractant tributyl phosphate. The subject has recently been extensively reviewed.<sup>1</sup> By comparison, anionic chelating ligands involving one or more P=O group have received little attention. Amongst the simplest of these are bidentate monophosphorylmonocarboxylates, and the co-ordination of 2-(diphenylphosphinoyl)acetate to organotin(IV) centres has been studied by Ng and Zuckerman.<sup>2</sup> This apart, no other complexes of  $\alpha$ -phosphinoylcarboxylates have been reported.

We report here the one-stage synthesis of 2-(diphenylphosphinoyl)propanoic acid, Hdpop, and an examination of some metal complexes of its anion. Our interest stems from the desire to make stable complexes of metals in high oxidation numbers as potential oxidation catalysts. Towards this end, 2-(diphenylphosphinoyl)propanoate offers the advantages of hard donor atoms suited to metals in high oxidation levels, resistance to oxidation, and the potential of resolution into its single enantiomers for extension to chiral oxidations.

### Experimental

The NMR spectra were recorded on a Bruker AM 200 spectrometer operating in the Fourier-transform mode, IR spectra on a Phillips PU 9800 spectrometer and UV/VIS spectra on a Perkin-Elmer Lambda 9. Microanalyses were carried out by Glasgow University Chemistry Department microanalytical service.

### Preparations

**(*R,S*)-2-(Diphenylphosphinoyl)propanoic acid (Hdpop).** To a stirred solution of diphenylphosphine oxide (9 g, 0.045 mol) in  $Me_2SO$  (50  $cm^3$ ) was added dropwise a 50% solution of KOH in water (11.96  $cm^3$ , 0.108 mol). The distinctive yellow colour of the diphenylphosphine oxide anion was formed on addition. To this mixture was added 2-chloropropanoic acid (4.8 g, 0.045 mol) dropwise with vigorous stirring. The temperature of the mixture rose to *ca.* 50 °C during the addition, and was maintained for 3 h. The mixture was poured into water (400

$cm^3$ ) and extracted once with benzene (200  $cm^3$ ). The aqueous phase was acidified with 2 mol  $dm^{-3}$  HCl, and the oily residue extracted into chloroform (2 × 200  $cm^3$ ). After drying the organic phase over anhydrous  $MgSO_4$ , the solvent was removed *in vacuo* to give an oil which was crystallised from  $CHCl_3$ –cyclohexane–hexane (1:2:3; 300  $cm^3$ ) then further recrystallised from hot toluene to give the desired compound as colourless needles. Yield = 9 g (73%), m.p. = 145–147 °C (lit.,<sup>3</sup> 138–140 °C) (Found: C, 65.6; H, 5.5. Calc. for  $C_{15}H_{15}O_3P$ : C, 65.7; H, 5.5%). IR (KBr): 3200–2300 (vbr), 1748vs, 1588w, 1485w, 1455w, 1439vs, 1391w, 1296s, 1229vs, 1159vs, 1117vs, 1099s, 997m, 988m, 843s, 758m, 721vs, 694vs, 583m, 552vs, 511vs and 432m  $cm^{-1}$ .

**Tl(dpop)·H<sub>2</sub>O.** Thallium(I) ethoxide (1.82 g, 7.3 mmol) was added with vigorous stirring to a solution of Hdpop (2 g, 7.3 mmol) in ethanol (25  $cm^3$ ). The solution was stirred for 3 h under nitrogen. The solvent was removed *in vacuo*, and the resultant gum crystallised from hot toluene. Yield = 2.5 g (72%) (Found: C, 36.4; H, 3.3. Calc. for  $C_{15}H_{16}O_4PTl$ : C, 36.35; H, 3.25%). IR (KBr): 3054w, 2966w, 2926w, 1570vs, 1456s, 1384s, 1340vs, 1168vs, 1116s, 1070m, 1004m, 888m, 817w, 725s, 703s, 558vs and 522vs  $cm^{-1}$ .

**V(dpop)<sub>3</sub>·H<sub>2</sub>O·CH<sub>2</sub>Cl<sub>2</sub>.** To a stirred suspension of  $VCl_3$  (50 mg, 0.32 mmol) in dry dichloromethane (15  $cm^3$ ) under nitrogen was added, as a solid,  $Tl(dpop)$  (459 mg, 0.96 mmol). Dry tetrahydrofuran (thf) (10  $cm^3$ ) was added, and the suspension stirred for 2 d. The precipitated  $TlCl$  was filtered off in air, and the green solution taken to dryness *in vacuo*. The resultant solid was precipitated from  $CH_2Cl_2$  upon addition of light petroleum (b.p. 40–60 °) and recrystallised from toluene–dichloromethane at 4 °C to give air-stable lime-green crystals suitable for X-ray analysis. Yield = 200 mg (72%) (Found: C, 56.5; H, 4.7. Calc. for  $C_{46}H_{46}Cl_2O_{10}P_3V$ : C, 56.75; H, 4.75%). IR (KBr): 3600w, 3432w, 3058w, 3006w, 2984w, 2938w, 2894w, 1676vs, 1654vs, 1624vs, 1588m, 1484w, 1436s, 1380m, 1308vs, 1250s, 1204m, 1124vs, 1068vs, 994m, 884s, 792s, 742s, 696vs, 606s, 526s, 496m and 432m  $cm^{-1}$ . UV/VIS ( $CH_2Cl_2$ ):  $\lambda_{max}/nm$  667 ( $\epsilon$  41) and 454 (59  $dm^3 mol^{-1} cm^{-1}$ ).

**Cr(dpop)<sub>3</sub>·H<sub>2</sub>O.** This complex was prepared in an analogous fashion to the that of  $V(dpop)_3$ , using  $[CrCl_3(thf)_3]$  as the

starting material. The green solid product was precipitated from dichloromethane upon addition of light petroleum (b.p. 40–60 °C). Yield = 50% (Found: C, 60.3; H, 5.1. Calc. for  $C_{45}H_{44}CrO_{10}P_3$ : C, 60.75; H, 5.0%). IR (KBr): 3442 (br), 3056w, 2982w, 2936w, 1648vs, 1438m, 1378w, 1308s, 1246w, 1124vs, 1068m, 996w, 888m, 790m, 746m, 694m, 600m, 532m, 504w and 446w  $cm^{-1}$ . UV/VIS ( $CH_2Cl_2$ ):  $\lambda_{max}/nm$  627 ( $\epsilon$  75) and 442 ( $91 dm^3 mol^{-1} cm^{-1}$ ).

**Fe(dpop)<sub>3</sub>·H<sub>2</sub>O·CH<sub>2</sub>Cl<sub>2</sub>.** Iron(III) tris(acetylacetonate) [ $Fe(acac)_3$ ] (100 mg, 0.28 mmol) was dissolved in dry thf (30  $cm^3$ ), to which was added Hdpop (230 mg, 0.84 mmol) as a solid. The mixture was stirred for 3 d under nitrogen. Dry diethyl ether (30  $cm^3$ ) was added, and the mixture was stored at 4 °C overnight. The orange precipitate was filtered off, washed with ether, and air-dried. Recrystallisation was effected from toluene–dichloromethane at 4 °C over several days. The crystalline golden-brown solid was filtered off, washed sparingly with toluene and air-dried. Yield = 230 mg (95%) (Found: C, 56.7; H, 4.8. Calc. for  $C_{46}H_{46}Cl_2FeO_{10}P_3$ : C, 56.45; H, 4.75%). IR (KBr): 3608w, 3432w, 3056w, 3006w, 2984w, 2958w, 2894w, 1674vs, 1654vs, 1622vs, 1588m, 1484m, 1436s, 1380m, 1304vs, 1250s, 1204m, 1124vs, 1062vs, 994m, 880s, 792s, 742s, 696vs, 602m, 524s, 494m and 422m  $cm^{-1}$ . UV/VIS ( $CH_2Cl_2$ ):  $\lambda_{max}/nm$  432 (sh) ( $\epsilon$  54  $dm^3 mol^{-1} cm^{-1}$ ).

**SnPh<sub>3</sub>(dpop).** To a stirred solution of Hdpop (0.3 g, 1.1 mmol) in ethanol (20  $cm^3$ ) was added triphenyltin(IV) chloride (0.385 g, 1.1 mmol). After complete dissolution, 1 mol equivalent of triethylamine was added, and the solution stirred for 1 h. The light suspension was filtered with the aid of Celite, and the filtrate taken to dryness *in vacuo*. The residue was dissolved in benzene, and filtered to remove triethylamine hydrochloride. Concentration of the benzene solution gave the desired complex which was recrystallised from dichloromethane as colourless crystals. Yield = 275 mg (40%), m.p. = 203–204 °C (Found: C, 63.4; H, 4.5. Calc. for  $C_{33}H_{29}O_3PSn$ : C, 63.6; H, 4.7%). IR (KBr): 3067w, 3052w, 1645vs, 1482w, 1429m, 1372m, 1337s, 1258m, 1202w, 1132s, 1118m, 1086s, 1024w, 997w, 810w, 731vs, 693vs, 571w, 525m and 455m  $cm^{-1}$ .

**SnMe<sub>3</sub>(dpop).** The compound Hdpop (210 mg, 0.77 mmol) and trimethyltin(IV) chloride (150 mg, 0.77 mmol) were added to a Schlenk tube under nitrogen. Dry thf (30  $cm^3$ ) was added, and the mixture stirred. After 0.5 h, 1 mol equivalent of potassium *tert*-butoxide was added, and the mixture stirred for 2 h. It was then pumped dry, and the residue stirred overnight with toluene (15  $cm^3$ ) and dichloromethane (15  $cm^3$ ). The insoluble salts were filtered off, and the dichloromethane removed *in vacuo* until a white solid precipitated. This was filtered off, washed with toluene then ether, air-dried and then reprecipitated from  $CH_2Cl_2$  upon addition of ether. Yield = 280 mg (83%), m.p. = 169–170 °C (Found: C, 49.2; H, 5.3. Calc. for  $C_{18}H_{23}O_3PSn$ : C, 49.45; H, 5.3%). IR (KBr): 3057m, 2990m, 2977m, 2936m, 2919m, 1634vs, 1439s, 1375s, 1339vs, 1177vs, 1119s, 1082m, 1074m, 1028w, 999w, 882m, 787vs, 723s, 694s, 556vs, 519vs and 436m  $cm^{-1}$ .

**SnPh<sub>2</sub>(dpop)<sub>2</sub>·3H<sub>2</sub>O.** To diphenyltin(IV) dichloride (100 mg, 0.29 mmol) in dry dichloromethane (25  $cm^3$ ) under nitrogen was added, with stirring, solid Tl(dpop) (277 mg, 0.58 mmol). The resultant mixture was stirred for 3 h, then filtered. The filtrate was concentrated *in vacuo*, and the product crystallised on addition of toluene–hexane (1:1). Some difficulty was encountered in the formation of a solid, as the compound tended to form a gum. The solid was reprecipitated from toluene–ethanol after several days. Yield = 75 mg (35%), m.p. 127–129 °C (Found: C, 57.8; H, 4.8. Calc. for  $C_{42}H_{44}O_9P_2Sn$ : C, 57.75; H, 5.1%). IR (KBr): 3448w, 3184w, 3062w, 3046w,

2968w, 2934w, 2870w, 1654m, 1634vs, 1482m, 1436s, 1430s, 1376s, 1334s, 1258m, 1176m, 1132s, 1118s, 1086vs, 1050m, 1024m, 998m, 886m, 812m, 750m, 732vs, 692vs, 570m, 554m, 526s, 456m, 448m and 408w  $cm^{-1}$ .

**SnMe<sub>2</sub>(dpop)<sub>2</sub>·3H<sub>2</sub>O.** This complex was prepared in a similar fashion to that of  $SnMe_3(dpop)$ . It was crystallised from toluene. Yield = 70%, m.p. = 98–100 °C (Found: C, 51.6; H, 5.0. Calc. for  $C_{32}H_{40}O_9P_2Sn$ : C, 51.3; H, 5.4%). IR (KBr): 3424 (br), 3056w, 2977w, 2936w, 1624 (br), 1456w, 1439vs, 1383m, 1338s, 1188s, 1119vs, 887w, 800m, 749m, 721s, 694vs, 558s and 527vs  $cm^{-1}$ .

**[MoO<sub>2</sub>(dpop)<sub>2</sub>].** To a stirred suspension of  $MoO_2Cl_2$  (100 mg, 0.50 mmol) in dry dichloromethane (25  $cm^3$ ) under nitrogen was added Tl(dpop) (682 mg, 1 mmol). The mixture was stirred for 2 d, and the precipitated TlCl filtered off. The blue filtrate was taken to dryness *in vacuo*, and the resultant solid boiled in toluene– $CH_2Cl_2$  (2:1; 30  $cm^3$ ) for 2 h. After cooling overnight, the very pale blue solid was filtered off, washed with toluene, then diethyl ether and air-dried. Yield = 200 mg (30%). (Found: C, 52.4; H, 4.0. Calc. for  $C_{30}H_{14}MoO_6P_2$ : C, 53.4; H, 4.2%). IR (KBr): 3064w, 2994w, 2944w, 2866w, 1702s, 1682vs, 1648m, 1588m, 1436s, 1382m, 1292s, 1258m, 1204vs, 1174vs, 1126vs, 1092m, 1066vs, 1028w, 996m, 936vs, 904vs, 894vs, 788m, 780m, 752s, 736m, 720m, 694s, 590s, 568m, 528m, 510s, 472w and 402w  $cm^{-1}$ .

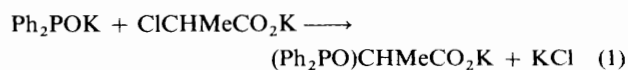
### Crystal structure determination of $V(dpop)_3 \cdot H_2O \cdot CH_2Cl_2$ 1

Details of the data collection procedures and structure refinement are given in Table 1. Crystals of complex **1**, were obtained as green prisms. A single crystal of suitable size was attached to a glass fibre using acrylic resin, and mounted on a goniometer head in a general position. Data were collected on an Enraf-Nonius TurboCAD4 diffractometer, running under CAD4-Express software, and using graphite-monochromated X-radiation ( $\lambda = 0.710 69 \text{ \AA}$ ). Precise unit-cell dimensions were determined by refinement of the setting angles of 25 high-angle reflections which were flagged during data collection. Standard reflections were measured every 2 h during data collection, and a small decay of *ca.* 5% was noted; an interpolated correction was applied to the reflection data. Lorentz-polarisation corrections and a semiempirical absorption correction (DIFABS)<sup>4</sup> were applied to the reflection data. The structure was solved by direct methods (SHELXS 86).<sup>5</sup> All non-H atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions, with C–H 0.96 Å. A molecule of water and of dichloromethane of solvation were also found. Refinement (SHELXL 93)<sup>6</sup> was by full-matrix least squares on  $F^2$ , using the weighting scheme  $w = [\sigma^2(F_o)^2 + (0.0576P)^2]^{-1}$  where  $P = [F_o^2/3 + 2F_c^2/3]$ ;  $\sigma(F_o)^2$  was estimated from counting statistics. Neutral atom scattering factors, anomalous dispersion coefficients and absorption coefficients were obtained from ref. 7. Fractional atomic coordinates are given in Table 2 with estimated standard deviations (e.s.d.s) in parentheses.

Complete atom coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

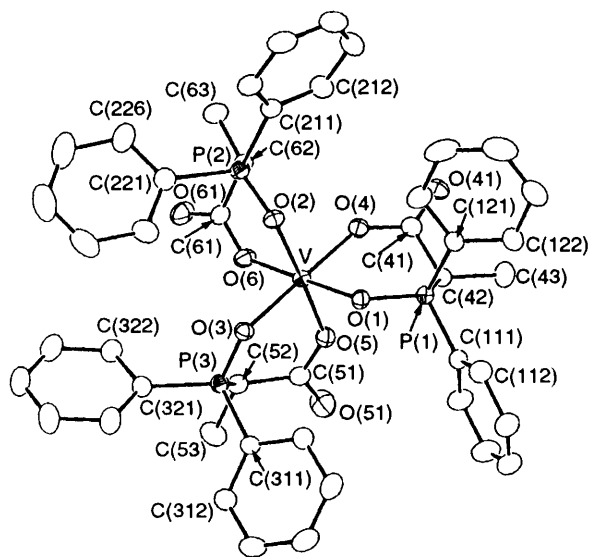
### Results and Discussion

2-(Diphenylphosphinoyl)propanoic acid, was conveniently made in excellent yield by treating the  $Ph_2PO^-$  anion with 2-chloropropanoic acid in alkaline solution [equation (1)], then



**Table 1** Experimental details of the crystal structure determination of  $V(\text{dpop})_3 \cdot \text{H}_2\text{O} \cdot \text{CH}_2\text{Cl}_2$ 

Formula	$\text{C}_{46}\text{H}_{46}\text{Cl}_2\text{O}_{10}\text{P}_3\text{V}$
$M_r$	973.58
Space group	$P2_1/c$
Crystal system	Monoclinic
$a/\text{\AA}$	15.0333(6)
$b/\text{\AA}$	14.1171(5)
$c/\text{\AA}$	21.6975(13)
$\beta/^\circ$	97.287(4)
$V/\text{\AA}^3$	4567.6(4)
$\theta$ Range for cell/ $^\circ$	17.5–21.3
$Z$	4
$D_c/\text{g cm}^{-3}$	1.416
$F(000)$	2016
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	4.96
Scan mode	$\omega$ -2 $\theta$
$\omega$ -Scan angle/ $^\circ$	$0.46 + 0.56 \tan \theta$
$\theta$ Range/ $^\circ$	2.1–25.0
Crystal size/mm	$0.33 \times 0.33 \times 0.13$
Range of transmission coefficients/corrections	1.09–0.84
No. data collected	8344
No. unique data	8018
$hkl$ Ranges	–17 to 0, 0–16, –25 to 25
$R_{\text{sigma}}$	0.054
Standard reflections	(–7, –1, 3), (–2, 1, 11), (–2, –7, –2)
No. data refined	8018
No. refined parameters	579
$R [I > 2\sigma(I)]$ (all data)	0.039 (0.075)
$R^2 [I > 2\sigma(I)]$ (all data)	0.097 (0.105)
Goodness of fit, $S$	1.021
Largest remaining features in electron-density map/ $e \text{\AA}^{-3}$	0.27, –0.38
Shift/ $e.s.d.$ in last cycle	0.0005 (mean), 0.003 (maximum)

**Fig. 1** Molecular structure and atomic labelling scheme of  $V(\text{dpop})_3$  with thermal ellipsoids at the 30% probability level

acidifying a method which has been used successfully to synthesise  $(\text{Ph}_2\text{PO})\text{CH}_2\text{CO}_2\text{H}$ .<sup>2,8</sup> The infrared spectrum of Hdpop reveals that the  $\nu(\text{P}=\text{O})$  stretch is shifted to low frequency through hydrogen bonding to the carboxylic acid group, the major band being assigned at  $1159 \text{ cm}^{-1}$ . The O–H stretch extends over the range  $3200$ – $2400 \text{ cm}^{-1}$ , again showing a low-frequency shift. The acid has previously been synthesised from the action of ethyllithium on triphenylphosphine oxide followed by treatment with  $\text{CO}_2$ , but its properties were not examined.<sup>3</sup>

Treatment of Hdpop with thallium(I) ethoxide readily produces crystalline  $\text{Tl}(\text{dpop})$ . The IR spectrum of the thallium(I) salt is less complex in the  $\nu(\text{P}=\text{O})$  region than that of Hdpop, with a single band (slight shoulder to high frequency) at

$1168 \text{ cm}^{-1}$ . The formation of this salt is accompanied by a shift to low frequency of  $\nu_{\text{asym}}(\text{C}=\text{O})$  of the carboxylate group by  $178 \text{ cm}^{-1}$ . Such lowering of carboxylate stretching bands has been interpreted in the analogous (diphenylphosphinoyl)acetate compound,  $(\text{Ph}_2\text{PO})\text{CH}_2\text{CO}_2\text{Ti}$ , as indicative of a polymeric structure involving strong interactions with both carboxylate oxygens.<sup>2</sup>

#### Complexes of the type $M(\text{dpop})_3$

The complexes  $V(\text{dpop})_3$  and  $\text{Cr}(\text{dpop})_3$  were readily synthesised from  $\text{VCl}_3$  or  $[\text{CrCl}_3(\text{thf})_3]$ , respectively, on treatment with  $\text{Tl}(\text{dpop})$ ;  $[\text{Fe}(\text{dpop})_3]$  was more conveniently synthesised from  $[\text{Fe}(\text{acac})_3]$  and the acid Hdpop. All complexes were obtained in good yield, and were readily recrystallised from toluene– $\text{CH}_2\text{Cl}_2$  at  $4^\circ\text{C}$ . Both the vanadium(III) and iron(III) complexes gave crystals suitable for X-ray analysis, and the structure of  $V(\text{dpop})_3 \cdot \text{OH}_2 \cdot \text{CH}_2\text{Cl}_2$  was thus established. The IR spectra of the vanadium and iron complexes were identical in every respect, so it was assumed that the iron compound would have essentially the same structural features and it was not examined crystallographically. The complex  $\text{Cr}(\text{dpop})_3$  does not crystallise as readily as the iron and vanadium analogues, and did not form a dichloromethane adduct.

The molecular structure of the  $V(\text{dpop})_3$  unit of compound **1** is shown in Fig. 1, with selected bond lengths and angles in Table 3. To our knowledge only two tris(oxygen chelate) complexes of  $\text{V}^{\text{III}}$  have been structurally characterised before,<sup>9,10</sup> and this is the first documented structure of any metal complex of a phosphinoyl carboxylate ligand. The complex has the expected octahedral geometry, with three bidentate dpop ligands. The V–O(P) bond lengths, averaging  $2.023(2) \text{ \AA}$ , are slightly longer than those of V–O(C) [averaging  $1.979(2) \text{ \AA}$ ] and this produces a minor source of distortion from ideal octahedral co-ordination geometry. These values are in the normal range for  $\text{V}^{\text{III}}$ –O bond lengths. The average V–O bond distance in  $[\text{V}(\text{OH}_2)_6]^{3+}$  is  $1.998(1) \text{ \AA}$ ,<sup>11</sup> and  $1.980$  and

**Table 2** Atomic coordinates ( $\times 10^4$ ) for complex **1**

Atom	x	y	z	Atom	x	y	z
V	7 410(1)	7 996(1)	1 479(1)	C(116)	5 418(2)	8 138(2)	3 071(2)
P(1)	6 421(1)	6 890(1)	2 472(1)	C(121)	6 708(2)	5 675(2)	2 604(1)
P(2)	8 880(1)	6 806(1)	884(1)	C(122)	6 218(2)	5 074(2)	2 947(1)
P(3)	8 131(1)	10 013(1)	1 937(1)	C(123)	6 430(3)	4 124(2)	2 986(2)
O(1)	7 223(1)	7 445(1)	2 313(1)	C(124)	7 093(3)	3 770(3)	2 689(2)
O(1S)	6 179(2)	259(3)	4 992(2)	C(125)	7 577(3)	4 348(3)	2 346(2)
O(2)	8 461(1)	7 101(1)	1 452(1)	C(126)	7 389(2)	5 301(2)	2 308(1)
O(3)	8 266(1)	8 954(1)	1 914(1)	C(211)	9 037(2)	5 550(2)	901(1)
O(4)	6 585(1)	7 010(1)	1 079(1)	C(212)	8 296(2)	4 969(2)	742(2)
O(5)	6 427(1)	8 912(1)	1 522(1)	C(213)	8 368(3)	4 001(2)	849(2)
O(6)	7 640(1)	8 516(1)	671(1)	C(214)	9 162(3)	3 615(2)	1 114(2)
O(41)	5 542(2)	5 899(2)	941(1)	C(215)	9 894(2)	4 183(2)	1 265(2)
O(51)	5 641(2)	10 231(2)	1 451(1)	C(216)	9 847(2)	5 141(2)	1 151(1)
O(61)	8 153(2)	8 689(2)	-233(1)	C(221)	9 917(2)	7 417(2)	862(1)
Cl(1S)	6 408(1)	204(1)	9 746(1)	C(222)	10 107(2)	8 171(2)	1 264(2)
Cl(2S)	6 026(1)	2 202(1)	9 580(1)	C(223)	10 829(2)	8 751(2)	1 203(2)
C(1S)	5 581(3)	1 090(3)	9 675(2)	C(224)	11 352(3)	8 587(3)	739(2)
C(41)	5 904(2)	6 563(2)	1 236(1)	C(225)	11 188(2)	7 845(3)	348(2)
C(42)	5 531(2)	6 915(2)	1 821(1)	C(226)	10 479(2)	7 243(3)	407(2)
C(43)	4 684(2)	6 398(2)	1 957(2)	C(311)	7 890(2)	10 350(2)	2 696(1)
C(51)	6 350(2)	9 820(2)	1 464(1)	C(312)	7 980(2)	11 271(2)	2 919(1)
C(52)	7 196(2)	10 378(2)	1 383(1)	C(313)	7 748(2)	11 494(2)	3 498(1)
C(53)	7 042(2)	11 455(2)	1 371(2)	C(314)	7 417(2)	10 802(2)	3 852(1)
C(61)	7 981(2)	8 196(2)	196(1)	C(315)	7 301(2)	9 898(2)	3 629(1)
C(62)	8 146(2)	7 121(2)	185(1)	C(316)	7 547(2)	9 660(2)	3 055(1)
C(63)	8 471(2)	6 784(2)	-413(1)	C(321)	9 111(2)	10 622(2)	1 748(1)
C(111)	5 998(2)	7 373(2)	3 141(1)	C(322)	9 286(2)	10 616(2)	1 138(1)
C(112)	6 274(2)	7 028(2)	3 736(1)	C(323)	10 077(2)	11 000(2)	982(2)
C(113)	5 935(2)	7 431(3)	4 244(2)	C(324)	10 685(2)	11 393(2)	1 430(2)
C(114)	5 349(2)	8 168(3)	4 163(2)	C(325)	10 519(2)	11 407(2)	2 030(2)
C(115)	5 087(2)	8 529(2)	3 581(2)	C(326)	9 743(2)	11 018(2)	2 194(1)

**Table 3** Selected bond lengths (Å) and angles (°) for complex **1**

V-O(6)	1.972(2)	P(3)-C(311)	1.793(3)
V-O(5)	1.976(2)	P(3)-C(321)	1.798(3)
V-O(4)	1.989(2)	P(3)-C(52)	1.804(3)
V-O(3)	2.016(2)	O(4)-C(41)	1.285(3)
V-O(1)	2.023(2)	O(5)-C(51)	1.292(3)
V-O(2)	2.030(2)	O(6)-C(61)	1.289(3)
P(1)-O(1)	1.514(2)	O(41)-C(41)	1.223(3)
P(1)-C(121)	1.783(3)	O(51)-C(51)	1.210(3)
P(1)-C(111)	1.792(3)	O(61)-C(61)	1.214(3)
P(1)-C(42)	1.817(3)	C(41)-C(42)	1.534(4)
P(2)-O(2)	1.512(2)	C(42)-C(43)	1.529(4)
P(2)-C(211)	1.788(3)	C(51)-C(52)	1.525(4)
P(2)-C(221)	1.788(3)	C(52)-C(53)	1.538(4)
P(2)-C(62)	1.813(3)	C(61)-C(62)	1.539(4)
P(3)-O(3)	1.511(2)	C(62)-C(63)	1.521(3)
O(6)-V-O(5)	90.88(8)	O(4)-V-O(1)	88.32(7)
O(6)-V-O(4)	92.47(8)	O(3)-V-O(1)	89.52(7)
O(5)-V-O(4)	92.85(8)	O(6)-V-O(2)	88.94(7)
O(6)-V-O(3)	89.63(7)	O(5)-V-O(2)	177.38(8)
O(5)-V-O(3)	88.59(7)	O(4)-V-O(2)	89.77(8)
O(4)-V-O(3)	177.43(8)	O(3)-V-O(2)	88.79(7)
O(6)-V-O(1)	177.82(8)	O(1)-V-O(2)	89.04(7)
O(5)-V-O(1)	91.10(7)		

2.013(9) Å in the tris(chelate) complexes  $[\text{V}(\text{acac})_3]^{-9}$  and  $[\text{V}(\text{cat})_3]^{3-}$  ( $\text{H}_2\text{cat} = \text{catechol}$ ),<sup>10</sup> respectively. The V-O(P) and P-O distances of 2.023 and 1.512 Å, respectively, in  $\text{V}(\text{dpop})_3$  fall between those reported for  $[\text{VCl}_3(\text{PMe}_2\text{Ph})_2(\text{OPMe}_2\text{Ph})]$  (1.966 and 1.520 Å) and  $[\text{VCl}_3(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)(\text{OPMe}_2\text{Ph})]$  (2.049 and 1.502 Å),<sup>12</sup> with an inverse relationship between the two lengths. The V-O(P) distances in the phosphine complexes were assigned to ligand *trans* effects, but the smaller V-O-P angles in  $\text{V}(\text{dpop})_3$  (127°) compared to those in the complexes of the monodentate phosphine oxide ligands (157.4 and 134.6°, respectively) would indicate that caution should be exercised before extending such conclusions to  $\text{V}(\text{dpop})_3$ .

The geometry about the metal ion in  $\text{V}(\text{dpop})_3$  is *fac*, and the absolute configuration as shown in the figure is  $\Lambda$ , with the chiral carbons of all three ligands possessing the *R* stereochemistry. The  $\Delta$  isomer is similarly stereospecific for the *S* form of the ligand, and the mirror image  $\Delta(S,S,S)$  unit has equal prevalence in the racemic crystal. All the O-V-O bond angles in the  $\text{V}(\text{dpop})_3$  unit are  $90 \pm 3^\circ$ , with the six-membered chelate rings producing bite angles averaging  $88.62(7)^\circ$ . These compare with  $87.6^\circ$  in the tris(acetylacetonate) complex<sup>9</sup> and  $85.4^\circ$  for the N-V-O angles of the six-membered rings in the tris(salicylaldehyde hydrazone) complex of  $\text{V}^{\text{III}}$ .<sup>13</sup>

Unusually, the six-membered chelate rings adopt boat conformations. This appears to be a consequence of the bulky diphenylphosphoryl units; the aromatic rings extend away from the metal in the complex, but would be sterically congested if even a single chair conformation was adopted. The central methyl groups project in a pseudo-equatorial fashion, true equatorial being precluded by the adoption of the boat conformation. Each  $\text{CO}_2^-$  group, its central carbon and the methyl carbon are essentially coplanar ( $< 3^\circ$  deviation).

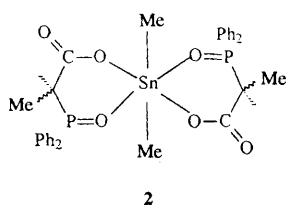
Two O(41) to O(S) distances of 2.87 and 3.21 Å were computed, indicating that the lattice water molecule bridges two  $\text{V}(\text{dpop})_3$  units by weak hydrogen bonds. The C(41)-O(41) length of 1.223(3) Å is 0.01 Å longer than the comparable bonds in the other two (dpop) ligands. There are no unusually close approaches involving the atoms of the lattice  $\text{CH}_2\text{Cl}_2$ .

The IR spectra of the tris(chelate) complexes show smaller reductions in  $\nu(\text{C}=\text{O})$  than does the thallium(II) complex ( $\text{Cr}^{\text{III}}$  100;  $\text{V}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$ ,  $94 \text{ cm}^{-1}$ ) compared to  $\text{Hdpop}$ , though the comparison with the last two metals is complicated by the presence of three overlapping peaks in the region of interest. Like the thallium(II) salt, the  $\nu(\text{P}=\text{O})$  region is less complex for the  $\text{M}(\text{dpop})_3$  species than  $\text{Hdpop}$ , with  $\Delta\nu(\text{P}=\text{O}) = -35 \text{ cm}^{-1}$  irrespective of the metal ion. The complexes of  $\text{Fe}^{\text{III}}$  and  $\text{V}^{\text{III}}$  have two distinct peaks for the  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}(\text{HOH})$  stretches of the lattice water. The spectrum of the iron complex is

**Table 4** The NMR data ( $\delta$ , J/Hz) for Hdpop and dpop complexes

Compound	$^1\text{H}$	$^{13}\text{C}$	$^{31}\text{P}$
Hdpop <sup>a</sup>	1.34 (dd, <i>J</i> 16.0, 7.2) 3.50 (dq, <i>J</i> 12.4, 7.2) 7.29–7.76 (Ph)	11.3 (d, <i>J</i> 4), 42.0 (d, <i>J</i> 62), 128.3 (d, <i>J</i> 12), 128.5 (d, <i>J</i> 12), 131.2 (d, <i>J</i> 11), 131.5 (d, <i>J</i> 11), 132.3, 171.8	34.5
SnPh <sub>3</sub> (dpop) <sup>a</sup>	1.40 (dd, <i>J</i> 15.6, 7.2) 3.65 (dq, <i>J</i> 14.4, 7.2) 7.2–7.7 (Ph)		32.5
SnMe <sub>3</sub> (dpop) <sup>b</sup>	0.21(s) <sup>c</sup> 1.29 (dd, <i>J</i> 16.6, 7.4) 3.47 (dq, <i>J</i> 14.6, 7.2) 7.15–7.80 (Ph)	0.6 <sup>d</sup> , 14.2 (d, <i>J</i> 4), 46.0 (d, <i>J</i> 65), 132.0 (d, <i>J</i> 12), 132.3 (d, <i>J</i> 12), 134.7 (d, <i>J</i> 11), 135.4 (d, <i>J</i> 11), 135.7 (d, <i>J</i> 10), 177.8	36.7
SnMe <sub>2</sub> (dpop) <sub>2</sub> <sup>a</sup>	0.46 (s) <sup>c</sup> 1.30 (dd, <i>J</i> 16.4, 7.2) 3.48 (dq, <i>J</i> 16.4, 7.2) 7.1–7.8 (Ph)	9.2, 11.9 (d, <i>J</i> 3), 42.0 (d, <i>J</i> 63), 128.4 (d, <i>J</i> 12), 128.6 (d, <i>J</i> 12), 131.1 (d, <i>J</i> 11), 131.4 (d, <i>J</i> 11), 132.0, 175.2	35.1
Tl(dpop)	1.37 (dd, <i>J</i> 17.2, 7.3) 3.54 (dq, <i>J</i> 7.3, 7.3) 7.46–7.94 (Ph)		41.5
[MoO <sub>2</sub> (dpop) <sub>2</sub> ] <sup>d</sup>	1.36 (dd, <i>J</i> 16.0, 7.1) 3.93 (dq, <i>J</i> 18.6, 7.2) 7.51–7.87 (Ph)	8.5 (d, <i>J</i> 4), 40.0 (d, <i>J</i> 62), 132.2 (d, <i>J</i> 12), 132.5 (d, <i>J</i> 12), 134.8 (d, <i>J</i> 9), 136.2 (m)	38.7

<sup>a</sup> In CDCl<sub>3</sub>. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>-MeOD. <sup>c</sup>  $|^2J(^{117/119}\text{Sn}-\text{Me})| = 63.9, 66.8$  Hz. <sup>d</sup> In MeOD. <sup>e</sup>  $|^2J(^{117/119}\text{Sn}-\text{Me})| = 93.7$  Hz.



indistinguishable from that of V(dpop)<sub>3</sub>, and it is therefore concluded that the crystal and molecular symmetry is analogous to those of the latter.

Electronic spectroscopic data are given in the Experimental section. As expected for high-spin d<sup>5</sup>, the iron complex has practically no discernible d-d features, merely a slight shoulder to high  $\lambda$  of the major charge-transfer band. The vanadium and chromium spectra each contain two observable d-d transitions of low intensity. These are the  $^3T_{1g} \rightarrow ^3T_{2g}$  and  $^3T_{1g} \rightarrow ^3T_{1g}(P)$  transitions for V<sup>III</sup> and  $^4A_{1g} \rightarrow ^4T_{2g}$  and  $^4A_{1g} \rightarrow ^4T_{1g}$  for Cr<sup>III</sup>. The positions of these  $\lambda_{\text{max}}$  are to high wavelength of the comparable transitions in [V(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>,<sup>14</sup> [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup><sup>15</sup> and [Cr(acac)<sub>3</sub>]<sup>16</sup> respectively.

#### Tin(IV) complexes of dpop

Interest in the biocidal properties of organotin compounds led Ng and Zuckerman<sup>2</sup> to examine the organotin(IV) diphenylphosphinoylacetates SnR<sub>3</sub>(OCOCH<sub>2</sub>POPh<sub>2</sub>) and SnR<sub>2</sub>(OCOCH<sub>2</sub>POPh<sub>2</sub>)<sub>2</sub> (R = Ph or Me). We have prepared the analogous dpop derivatives by treatment of the respective organotin chlorides by Hdpop and base or by Tl(dpop). The compounds are white, diamagnetic solids, the mono(dpop) systems being readily recrystallised from organic solvents, the SnR<sub>2</sub>(dpop)<sub>2</sub> complexes being less well behaved, with SnPh<sub>2</sub>(dpop)<sub>2</sub> having very low solubility in all common solvents.

As emphasised by Ng and Zuckerman,<sup>2</sup> three stretching modes in the infrared spectra of complexes of this type are of potential benefit for deducing the nature of the co-ordination of these ligands. These are the  $\nu(\text{CO}_2)$ ,  $\nu(\text{P}=\text{O})$  and  $\nu(\text{Sn}-\text{C})$  stretching bands. The  $\nu_{\text{asym}}(\text{C}=\text{O})$  bands near 1640 cm<sup>-1</sup> are shifted by -103, -116, -114 and -120 cm<sup>-1</sup> for SnPh<sub>3</sub>(dpop), SnMe<sub>3</sub>(dpop), SnPh<sub>2</sub>(dpop)<sub>2</sub> and SnMe<sub>2</sub>(dpop)<sub>2</sub>, respectively, compared to that of Hdpop, all occurring at slightly lower frequency than for the M(dpop)<sub>3</sub> complexes. The major  $\nu(\text{P}=\text{O})$  stretching mode occurs to low frequency of that of Hdpop for the two phenyltin derivatives, but of high fre-

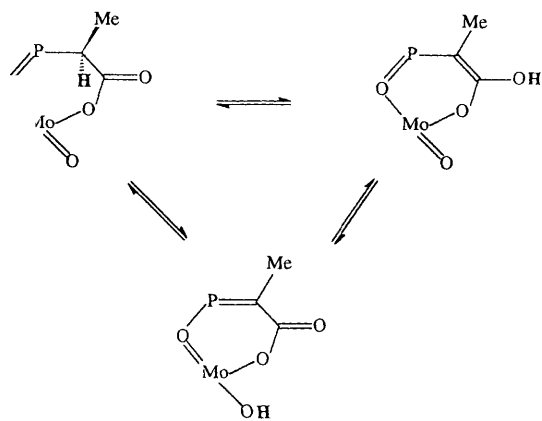
quency in the methyltin systems (though the number of bands in this region introduces some uncertainty in the assignments). All of these shifts correspond closely with those reported for the related complexes with diphenylphosphinoylacetate.<sup>2</sup>

The NMR data for the complexes are presented in Table 4. The chemical shift values for Hdpop and those of the dpop complexes are very similar, and are of little use in structural elucidation. The  $|^2J(^{119}\text{Sn}-^1\text{H})|$  coupling constants have been correlated with the Me-Sn-Me bond angle ( $\theta$ ) in a large number of organotin(IV) complexes.<sup>17</sup> Such a relationship has proved useful in determining the co-ordination number at tin. For SnMe<sub>2</sub>(dpop)<sub>2</sub>,  $J(\text{Sn}-\text{Me}) = 93.7$  Hz, giving a  $\theta$  value of 151° using the expression of Lockhart and Manders.<sup>17</sup> Such a value excludes the possibility of four co-ordinated tin with two monodentate dpop ligands, and is indicative of *trans* methyls as depicted in structure 2. Extensive line broadening occurs at 213 K in both the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of SnMe<sub>2</sub>(dpop)<sub>2</sub> as might be expected from the likely presence of *cis* and *trans* P=O isomers with *R,R/S,S* and *meso* forms of each. The average Me-Sn-Me angle in SnMe<sub>3</sub>(dpop) is calculated to be 117°, concordant with five-co-ordinate complexes of similar type.<sup>17</sup> No change in either the  $^1\text{H}$  or  $^{31}\text{P}$  NMR spectra of this compound occurs on cooling to 213 K.

The complexes SnMe<sub>2</sub>(dpop)<sub>2</sub>, SnPh<sub>3</sub>(dpop) and SnMe<sub>3</sub>(dpop) are thus probably monomeric like the analogous (diphenylphosphinoyl)acetates, with SnR<sub>3</sub>(dpop) being five-co-ordinate. The insoluble nature of SnPh<sub>2</sub>(dpop)<sub>2</sub> may indicate that this is a polymer with bridging dpop ligands, although its well resolved IR spectrum would indicate a high level of internal order in the solid.

#### *cis*-[MoO<sub>2</sub>(dpop)<sub>2</sub>] and H/D exchange

The reaction between MoO<sub>2</sub>Cl<sub>2</sub> and Tl(dpop) produces the complex [MoO<sub>2</sub>(dpop)<sub>2</sub>]. The two very strong IR bands at 936 and 904 cm<sup>-1</sup> are indicative of a *cis*-dioxomolybdenum geometry, and the highly resolved appearance of the rest of the IR spectrum, with many sharp bands, suggests a large degree of internal symmetry. The compound is insoluble in all the usual organic solvents except methanol and ethanol, and even here its solubility is low and with a slow rate of dissolution. Moreover the compound could not be recovered from solution in crystalline form. It thus appears to be polymeric in the solid phase as isolated, like SnPh<sub>2</sub>(dpop)<sub>2</sub>. Rearrangements to mononuclear forms on slow dissolution can result in the



Scheme 1

formation of a very large number of isomers, which may explain its reluctance to recrystallise.

The NMR spectral data for freshly dissolved *cis*-[MoO<sub>2</sub>(dpop)<sub>2</sub>] and Tl(dpop) in CD<sub>3</sub>OD are given in Table 4. Over a period of a few days a steady change is observed. The  $\alpha$ -hydrogen resonances near  $\delta$  3.7 diminish in intensity, while the CH<sub>3</sub> signals near  $\delta$  1.4 (dd) are converted into a simple doublet. The signal for the  $\alpha$ -carbon atoms diminishes in intensity at the same time. These changes are indicative of the loss of the  $\alpha$ -hydrogen atoms from the dpop ligands, and appear to be the result of H/D exchange with the deuteriomethanol solvent. The process is reversible. Addition of water to the sample of the thallium compound resulted in an equally slow regrowth of the  $\alpha$ -hydrogen signal in the spectrum.

The ability of the  $\alpha$ -hydrogens of Tl(dpop) and [MoO<sub>2</sub>(dpop)<sub>2</sub>] to undergo this type of exchange is probably the result of the operation of different processes. The thallium compound is likely to be quite ionic in character, and may well equilibrate with the  $\alpha$ -carbon bonded form Tl[CMe(POPh<sub>2</sub>)CO<sub>2</sub>H], rendering the migrating hydrogen atom quite acidic. In the molybdenum complex, hydrogen migrations of a different sort are more likely, as shown in Scheme 1. We note that if the six-membered rings of the Mo(dpop) units adopt the same boat conformations as do the V<sup>III</sup>(dpop) rings, this can allow a close approach of the  $\alpha$ -hydrogens to the Mo=O oxygens. These

migrations, too, would render the hydrogen atoms acidic and liable to exchange. Neither of these proposed mechanisms would apply to the tin compounds. No exchange was observed with the organotin compound SnMe<sub>3</sub>(dpop) in CD<sub>3</sub>OD.

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