Polymeric and Bimetallic Complexes of Diisopropyl Monothiophosphate†

Julian R. Phillips,[a] Julia C. Poat,[a] Alexandra M. Z. Slawin,[b] David J. Williams,[a] Paul T. Wood[a] and J. Derek Woollins *,[b]

[a] *Department of Chemistry, Imperial College, London SW7 2AY, UK*

[b] *Department of Chemistry, Loughborough University, Loughborough LE11 3TU, UK*

The single stage preparation of $M[O(S)P(OPr^i)_2]_n$ (n = 2, M = Zn **1**, Co **2** or Cd **3**; n = 1, M = NH_4^+ **4**) from $HPO(OPr^i)_2$, sulfur and ZnO, $CoCO_3$, $CdCO_3$ or NH_3 has been achieved. The reaction of **1** with *cis*-$[PtCl_2(PMe_2Ph)_2]$ and $[PPh_4][MCl_3(PMe_2Ph)]$ (M = Pt or Pd) gave $[(PMe_2Ph)_2Pt\{O(S)P(OPr^i)_2\}_2ZnCl_2]$ **5** and $[(PMe_2Ph)M\{O(S)P(OPr^i)_2\}_3ZnCl]$ (M = Pd **6** or Pt **7**) respectively. The crystal structures of **3**, **6** and **7** have been determined. The cadmium complex **3** exists as $Cd_2[O(S)P(OPr^i)_2]_3$ units linked by additional monothiophosphate ligands into polymeric chains. Complexes **6** and **7** are isomorphous and contain tetrahedral zinc centres linked to square-planar platinum atoms with polymer formation being inhibited by the presence of PMe_2Ph ligands.

Complexes of dialkyl dithiophosphates have been extensively studied.[1–3] One particular interest is in the chemistry of zinc dialkyl dithiophosphates which are used as lubricant additives because of their dual function as both anti-oxidant and anti-wear agents.[4] Typically zinc dialkyl dithiophosphates are prepared by reaction of an alcohol with P_4S_{10} [eqn. (1)]

$$4ROH + \tfrac{1}{2}P_4S_{10} \longrightarrow 2(RO)_2P(S)SH + H_2S \qquad (1)$$

followed by neutralisation of the resulting acid with zinc oxide [eqn. (2)], although the latter step is actually somewhat

$$2(RO)_2P(S)SH + ZnO \longrightarrow Zn[S_2P(OR)_2]_2 + H_2O \qquad (2)$$

more complex than indicated since a 'basic' form of zinc dialkyl dithiophosphate of composition $[Zn_4O\{S_2P(OR)_2\}_6]$ may also be formed. The interconversion of 'normal' into 'basic' zinc dialkyl dithiophosphate has been investigated[5–7] although the structure of the 'basic' compound has not yet been fully elucidated.[8,9]

Here, we describe the simple 'one-pot' synthesis of some diisopropyl monothiophosphate complexes $M[O(S)P(OPr^i)_2]_n$ (n = 2, M = Zn **1**, Co **2** or Cd **3**; n = 1, M = NH_4^+ **4**) as well as studies into their reactivity to form binuclear systems with platinum and palladium. A preliminary account[10] of the formation of $[(PMe_2Ph)_2Pt\{O(S)P(OPr^i)_2\}_2ZnCl_2]$ **5** and a related trinuclear complex have been reported.[11] The new compounds have been characterised by NMR, IR, microanalysis and in the case of **3** and $[(PMe_2Ph)M\{O(S)P(OPr^i)_2\}_3ZnCl]$ (M = Pd **6** or Pt **7**) by single-crystal X-ray studies.

Experimental

Starting materials were commercial materials (Aldrich or BDH). The complexes $[\{MCl_2(PMe_2Ph)\}_2]$ (M = Pt or Pd) were prepared by reaction of $[MCl_2(PMe_2Ph)_2]$ with MCl_2 in xylene at *ca.* 160°;[12] $[PPh_4][MCl_3(PMe_2Ph)]$ was prepared *in situ* by reaction of the dimers with 2 equivalents of $[PPh_4]Cl$.[13] Dichloromethane was dried and distilled over CaH_2 under nitrogen; hexane, $CDCl_3$ (98%), toluene and acetone were used as received. Proton (89.6 MHz), $^{31}P-\{^1H\}$, (109.4 and 202.5 MHz) and ^{195}Pt NMR spectra (57.9 MHz) were recorded ($CDCl_3$ solution) on JEOL FX90Q, JNM EX270 and Bruker AM500 FT spectrometers. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 1720X FT spectrometer. Microanalyses were carried out by the Imperial College Microanalytical Service.

Preparation of Zinc, Cadmium, Cobalt and Ammonium Diisopropyl Monothiophosphates.—In a typical reaction ZnO, $CdCO_3$ or $CoCO_3$ (12.5 mmol) was added to $HPO(OPr^i)_2$ (25 mmol, 4.16 g) and sulfur (25 mmol, 0.8 g) and refluxed in toluene (10 cm^3) for 4 h. The solution was allowed to cool and the toluene removed *in vacuo* to leave $M[O(S)P(OPr^i)_2]_2$. The crude product was washed with cold hexane and recrystallised from methanol. For the zinc salt 4% (by weight) of zinc acetate was also added to increase the rate of reaction and for the cobalt salt a further recrystallisation from acetone was also necessary.

The ammonium salt was prepared from the same mixture of sulfur and $HPO(OPr^i)_2$ in toluene. This was heated to 90 °C and ammonia passed through the solution for 1 h. The product was purified in the same way as for the metal salts.

$Zn[O(S)P(OPr^i)_2]_2$ **1**: yield 2.88 g, 50% (Found: C, 31.20; H, 6.05. Calc. for $C_{12}H_{28}O_6P_2S_2Zn$: C, 31.35; H, 6.15%). $Co[O(S)P(OPr^i)_2]_2$ **2**: yield 3.6 g, 68% (Found: C, 31.65; H, 6.20. Calc. for $C_{12}H_{28}CoO_6P_2S_2$: C, 31.80; H, 6.25%). $Cd[O(S)P(OPr^i)_2]_2$ **3**: yield 4.24 g, 71% (Found: C, 28.20; H, 5.55. Calc. for $C_{12}H_{28}CdO_6P_2S_2$: C, 28.45; H, 5.60%). $NH_4[O(S)P(OPr^i)_2]$ **4**: yield 4.15 g, 77% (Found: C, 33.10; H, 8.6; N, 6.55. Calc. for $C_6H_{18}NO_3PS$: C, 35.8; H, 8.95; N, 6.95%).

Reactions of $Zn[O(S)P(OPr^i)_2]_2$.—*With* $[PtCl_2(PMe_2Ph)_2]$. A mixture of $Zn[O(S)P(OPr^i)_2]_2$ (0.085 g) and $[PtCl_2(PMe_2Ph)_2]$ (0.1 g) was stirred in CH_2Cl_2 (2 cm^3) at room temperature for 24 h. The volume of the solution was reduced to *ca.* 1 cm^3 *in vacuo* and slow diffusion of hexane into this solution gave a pure crystalline sample of $[(PMe_2Ph)_2Pt\{O(S)P(OPr^i)_2\}_2ZnCl_2]$ **5**: yield 0.12 g, 60% (Found: C, 33.45; H, 4.90. Calc. for $C_{28}H_{50}Cl_2O_6P_4PtS_2Zn$: C, 33.55; H, 5.05%). ^{31}P NMR: δ 36.2 [$^2J(^{31}P-^{195}Pt)$ 65.9], −11.7 [$^1J(^{31}P-^{195}Pt)$ 3264 Hz].

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Details of the data collection and refinements*

Compound	**3**	**6**	**7**
Empirical formula	$C_{24}H_{56}Cd_2O_{12}P_4S_4$	$C_{26}H_{53}ClO_9P_4PdS_3Zn$	$C_{26}H_{53}ClO_9P_4PtS_3Zn$
Colour, habit	Clear prisms	Orange prisms	Yellow prisms
Crystal size/mm	0.23 × 0.28 × 0.37	0.134 × 0.200 × 0.266	0.133 × 0.234 × 0.434
Diffractometer	Siemens R3m/E	Siemens P4/PC	Siemens P4/PC
Radiation (λ/Å)	Cu-Kα (1.541 78)	Mo-Kα (0.710 73)	Mo-Kα (0.710 73)
a/Å	13.495(3)	12.728(3)	12.702(3)
b/Å	20.161(4)	20.849(4)	20.936(3)
c/Å	17.082(3)	15.903(3)	15.876(3)
β/°	98.59(3)	91.62(3)	91.64(2)
U/Å^3	4595.4	4218	4220.2
M	1013.6	937.0	1025.7
D_c/Mg m^{-3}	1.465	1.475	1.614
Absorption coefficient/mm^{-1}	10.81	1.40	4.28
2θ range/°	0.0–116	7.0–45.0	3.0–50.0
F(000)	2064	1928	2056
Ind. reflections (R_{int})	6192 (0.0)	7414 (0.0241)	7426 (0.0183)
Observed reflections [$F > 3.0\sigma(F)$]	4047	4824	5481
Data: parameter ratio	9.8:1	11.9:1	13.5:1
Min., max. transmission	0.151, 0.318	0.747, 0.847	0.376, 0.569
No. of parameters refined	415	406	407
Final R, R'	0.0948, 0.0901	0.0566, 0.0477	0.0419, 0.0366
Largest, mean Δ/σ	0.747, 0.082	2.341, 0.025	2.735, 0.033
Largest difference peak, hole/e Å^{-3}	1.39, −1.00	0.75, −0.82	0.87, −0.80

* Details in common: monoclinic, space group $P2_1/n$, $Z = 4$, face indexed absorption correction, weighting scheme $w^{-1} = \sigma^2(F) + 0.0003F^2$. Crystals of complex **1** are monoclinic, space group $P2_1/c$, a = 19.389(11), b = 22.332(13), c = 20.589(10) Å, β = 94.16(5)°, U = 8891 Å^3; **2** is isomorphous with **1**.

With $[PPh_4][PtCl_3(PMe_2Ph)]$. A mixture of $[PtCl_2(PMe_2Ph)_2]$ (0.1 g) and $[PPh_4]Cl$ (0.092 g) was dissolved in CH_2Cl_2 (20 cm^3) and, after stirring for 5 min, solid $Zn[O(S)P(OPr^i)_2]_2$ (0.2 g) was added. The resulting yellow solution was stirred for a further 15 min. The solvent was then removed under vacuum and the product extracted into pentane (50 cm^3). The pentane solution was reduced to *ca.* 5 cm^3 under vacuum and $[(PMe_2Ph)Pt\{O(S)P(OPr^i)_2\}_3ZnCl]$ **7** deposited as yellow crystals on cooling. The product was recrystallised from hexane; yield 0.172 g, 72% (Found: C, 30.30; H, 5.10. Calc. for $C_{26}H_{53}ClO_9P_4PtS_3Zn$ C, 31.7; H, 5.40%).

With $[PPh_4][PdCl_3(PMe_2Ph)]$. The reaction with $[PPh_4][PdCl_3(PMe_2Ph)]$ was performed as above using $[PdCl_2(PMe_2Ph)_2]$ (0.045 g), $[PPh_4]Cl$ (0.046 g) and $Zn[O(S)P(OPr^i)_2]_2$ (0.110 g). Complex $[(PMe_2Ph)Pd\{O(S)P(OPr^i)_2\}_3ZnCl]$ **6** was formed as orange crystals and recrystallised from pentane. Yield 0.108 g, 81% (Found: C, 33.35; H, 5.65. Calc. for $C_{26}H_{53}ClO_9P_4PdS_3Zn$: C, 34.90; H, 5.95%).

X-Ray Crystallography.—Details of the data collections and refinements are summarised in Table 1. All three structures were solved by direct methods and refined by full-matrix least-squares methods using anisotropic thermal parameters for the non-hydrogen atoms. The positions of the hydrogen atoms were idealised, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. In all three structures absorption corrections (face indexed numerical corrections) were applied. Computations were performed using the SHELXTL PC system.[14]

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

Results and Discussion

$$MCO_3 + 2HPO(OPr^i)_2 + \tfrac{2}{8}S_8 \longrightarrow M[O(S)P(OPr^i)_2]_2 + CO_2 + H_2O \quad (M = Co\ or\ Cd) \qquad (3)$$

$$ZnO + 2HPO(OPr^i)_2 + \tfrac{2}{8}S_8 \longrightarrow Zn[O(S)P(OPr^i)_2]_2 + H_2O \qquad (4)$$

$$NH_3 + HPO(OPr^i)_2 + \tfrac{1}{8}S_8 \longrightarrow NH_4[O(S)P(OPr^i)_2] \qquad (5)$$

The formation of metal monothiophosphate complexes proceeds smoothly in fair yield *via* a 'one-pot' method according to equations (3)–(5). If these reactions are conducted in two stages, *i.e.* with attempted isolation of the diisopropyl thiophosphoric acid, the oxidation at the phosphorus centre does not proceed to completion with yields of the acid varying from 30 to 50% (by NMR spectroscopy). The complex $Co[O(S)P(OPr^i)_2]_2$ is a bright blue crystalline solid which is soluble in a wide range of organic solvents, giving blue solutions in chlorinated and aromatic solvents and pink solutions in alcohols or water or in other strongly co-ordinating solvents such as tetrahydrofuran (thf). The ammonium salt and the zinc and cadmium complexes are colourless crystalline solids which are moderately soluble in most organic solvents.

The structure of complex **3** (Tables 2 and 3, Fig. 1) comprises pairs of tetrahedrally co-ordinated cadmium atoms linked *via* three monothiophosphate ligands to give Cd_2L_3 propeller-like 'cages'. These units are further linked *via* additional $OP(OPr^i)_2S^-$ ligands to give polymer chains. Each cadmium is bonded to two sulfur and two oxygen atoms. The tetrahedral geometry at each cadmium centre is severely distorted with angles in the ranges 96.7(5)–123.9(3)° at Cd(1) and 91.5(6)–121.1(5)° at Cd(2). The angles about the phosphorus atoms are unexceptional; those within the cage are noticeably enlarged from tetrahedral at 112.3(8)–113.6(6)° as is the S–P–O angle at P(4) in the ligand which links the Cd_2L_3 groups [116.2(10)°]. Similarly, the angles at sulfur are normal [93.8(3)–100.3(4)°]. The most striking angular distortions are seen for the P–O–Cd angles which, with the exception of O(1) [149.2(10)°], are closer to linear than trigonal [154.3(9)–163.2(11)°]. Although not common, angular distortions of this type have been noted before, *e.g.* in $[MoCl_4(NO)(PO_2Cl_2)]^{2-}$ the Mo–O–P angle is 169.5°.[15] There is no apparent reason for the enlargement of the angles at oxygen in complex **3**. The Cd(1) • • • Cd(1a) distance is

Table 2 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd(1)	1 616(1)	8 252(1)	10 066(1)	C(7)	3 546(14)	7 859(8)	8 396(10)
Cd(2)	223(1)	7 269(1)	8 202(1)	C(8)	3 605(22)	7 247(9)	7 908(18)
S(1)	−3(5)	8 399(4)	10 577(4)	C(9)	4 561(12)	8 171(14)	8 579(17)
P(1)	−933(5)	8 110(4)	9 640(4)	O(8)	1 456(10)	9 150(6)	7 599(8)
O(1)	−514(12)	7 573(7)	9 192(9)	C(10)	2 053(12)	9 718(7)	7 383(13)
S(2)	2 358(7)	9 097(3)	9 265(4)	C(11)	2 222(23)	9 615(15)	6 543(13)
P(2)	1 932(5)	8 626(3)	8 248(4)	C(12)	1 420(21)	10 328(6)	7 394(19)
O(2)	1 126(11)	8 146(7)	8 303(10)	O(9)	2 910(6)	6 155(6)	9 650(7)
S(3)	1 069(5)	6 209(3)	8 655(4)	C(13)	3 673(12)	6 230(9)	10 361(8)
P(3)	1 852(4)	6 504(3)	9 662(3)	C(14)	3 850(20)	5 558(13)	10 730(13)
O(3)	1 991(10)	7 258(5)	9 720(7)	C(15)	4 654(10)	6 368(19)	10 082(16)
S(4)	−614(7)	7 380(4)	6 835(4)	O(10)	1 459(13)	6 146(8)	10 395(8)
P(4)	−1 564(4)	6 640(3)	6 782(3)	C(16)	582(16)	6 408(12)	10 721(16)
O(4)	−2 425(14)	6 690(11)	6 204(10)	C(17)	895(30)	6 507(26)	11 592(16)
O(5)	−1 920(10)	7 794(11)	9 895(11)	C(18)	−221(17)	5 890(23)	10 596(24)
C(1)	−2 394(22)	7 794(14)	10 620(12)	O(11)	−1 778(15)	6 547(9)	7 666(6)
C(2)	−3 019(35)	7 179(22)	10 606(26)	C(19)	−2 603(16)	6 222(12)	7 999(16)
C(3)	−2 848(43)	8 466(19)	10 689(29)	C(20)	−3 444(17)	6 712(21)	7 958(20)
O(6)	−1 409(18)	8 724(8)	9 121(12)	C(21)	−2 210(28)	6 042(25)	8 840(16)
C(4)	−848(17)	9 240(15)	8 755(18)	O(12)	−1 104(19)	5 925(6)	6 670(14)
C(5)	−1 271(39)	9 899(9)	8 939(32)	C(22)	−254(14)	5 539(11)	6 454(16)
C(6)	−1 326(35)	9 307(21)	7 909(16)	C(23)	−681(31)	5 021(19)	5 869(22)
O(7)	2 886(9)	8 336(7)	7 908(8)	C(24)	18(29)	5 032(15)	7 093(21)

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

Cd(1)–S(1)	2.488(7)	Cd(1)–S(2)	2.489(8)	C(1)–C(2)	1.499(54)	C(1)–C(3)	1.498(51)
Cd(1)–O(3)	2.170(12)	Cd(1)–O(4a)	2.172(16)	O(6)–C(4)	1.479(35)	C(4)–C(5)	1.498(42)
Cd(2)–O(1)	2.175(17)	Cd(2)–O(2)	2.139(15)	C(4)–C(6)	1.498(41)	O(7)–C(7)	1.480(21)
Cd(2)–S(3)	2.491(6)	Cd(2)–S(4)	2.447(7)	C(7)–C(8)	1.497(29)	C(7)–C(9)	1.498(26)
S(1)–P(1)	1.969(9)	P(1)–O(1)	1.485(18)	O(8)–C(10)	1.478(21)	C(10)–C(11)	1.500(33)
P(1)–O(5)	1.596(18)	P(1)–O(6)	1.600(19)	C(10)–C(12)	1.499(25)	O(9)–C(13)	1.478(17)
S(2)–P(2)	1.987(9)	P(2)–O(2)	1.470(17)	C(13)–C(14)	1.499(30)	C(13)–C(15)	1.499(26)
P(2)–O(7)	1.601(15)	P(2)–O(8)	1.596(14)	O(10)–C(16)	1.479(29)	C(16)–C(17)	1.498(38)
S(3)–P(3)	1.971(8)	P(3)–O(3)	1.533(12)	C(16)–C(18)	1.496(42)	O(11)–C(19)	1.476(30)
P(3)–O(9)	1.596(11)	P(3)–O(10)	1.603(16)	C(19)–C(20)	1.499(40)	C(19)–C(21)	1.499(39)
S(4)–P(4)	1.960(11)	P(4)–O(4)	1.412(18)	O(12)–C(22)	1.478(32)	C(22)–C(23)	1.499(44)
P(4)–O(11)	1.590(13)	P(4)–O(12)	1.592(17)	C(22)–C(24)	1.501(41)		
O(4)–Cd(1a)	2.172(16)	O(5)–C(1)	1.476(31)				
S(1)–Cd(1)–S(2)	123.9(3)	S(1)–Cd(1)–O(3)	117.3(4)	S(4)–P(4)–O(11)	104.9(8)	O(4)–P(4)–O(11)	115.2(11)
S(2)–Cd(1)–O(3)	110.6(4)	S(1)–Cd(1)–O(4a)	96.7(5)	S(4)–P(4)–O(12)	115.5(10)	O(4)–P(4)–O(12)	106.0(12)
S(2)–Cd(1)–O(4a)	102.7(6)	O(3)–Cd(1)–O(4a)	99.3(6)	O(11)–P(4)–O(12)	97.9(12)	P(4)–O(4)–Cd(1a)	161.6(13)
O(1)–Cd(2)–O(2)	91.5(6)	O(1)–Cd(2)–S(3)	104.0(4)	P(1)–O(5)–C(1)	135.4(16)	O(5)–C(1)–C(2)	107.4(25)
O(2)–Cd(2)–S(3)	117.1(4)	O(1)–Cd(2)–S(4)	121.1(5)	O(5)–C(1)–C(3)	107.5(27)	C(2)–C(1)–C(3)	120.9(34)
O(2)–Cd(2)–S(4)	100.3(5)	S(3)–Cd(2)–S(4)	120.0(3)	P(1)–O(6)–C(4)	126.1(19)	O(6)–C(4)–C(5)	107.4(27)
Cd(1)–S(1)–P(1)	99.5(3)	S(1)–P(1)–O(1)	112.9(7)	O(6)–C(4)–C(6)	107.3(24)	C(5)–C(4)–C(6)	90.0(29)
S(1)–P(1)–O(5)	110.6(8)	O(1)–P(1)–O(5)	104.3(11)	P(2)–O(7)–C(7)	118.8(12)	O(7)–C(7)–C(8)	107.4(15)
S(1)–P(1)–O(6)	112.1(8)	O(1)–P(1)–O(6)	115.5(10)	O(7)–C(7)–C(9)	107.4(16)	C(8)–C(7)–C(9)	109.8(19)
O(5)–P(1)–O(6)	100.2(12)	Cd(2)–O(1)–P(1)	149.2(10)	P(2)–O(8)–C(10)	120.6(11)	O(8)–C(10)–C(11)	107.4(16)
Cd(1)–S(2)–P(2)	93.8(3)	S(2)–P(2)–O(2)	112.3(8)	O(8)–C(10)–C(12)	107.4(16)	C(11)–C(10)–C(12)	107.1(20)
S(2)–P(2)–O(7)	110.4(6)	O(2)–P(2)–O(7)	115.2(9)	P(3)–O(9)–C(13)	117.3(11)	O(9)–C(13)–C(14)	107.5(15)
S(2)–P(2)–O(8)	109.0(6)	O(2)–P(2)–O(8)	104.8(8)	O(9)–C(13)–C(15)	107.4(14)	C(14)–C(13)–C(15)	102.0(20)
O(7)–P(2)–O(8)	104.6(8)	Cd(2)–O(2)–P(2)	163.2(11)	P(3)–O(10)–C(16)	120.6(14)	O(10)–C(16)–C(17)	107.4(21)
Cd(2)–S(3)–P(3)	100.0(3)	S(3)–P(3)–O(3)	113.6(6)	O(10)–C(16)–C(18)	107.5(22)	C(17)–C(16)–C(18)	109.0(29)
S(3)–P(3)–O(9)	102.7(6)	O(3)–P(3)–O(9)	109.7(7)	P(4)–O(11)–C(19)	132.2(14)	O(11)–C(19)–C(20)	107.4(22)
S(3)–P(3)–O(10)	110.5(6)	O(3)–P(3)–O(10)	116.6(9)	O(11)–C(19)–C(21)	107.3(21)	C(20)–C(19)–C(21)	111.2(27)
O(9)–P(3)–O(10)	102.2(8)	Cd(1)–O(3)–P(3)	154.3(9)	P(4)–O(12)–C(22)	146.9(17)	O(12)–C(22)–C(23)	107.3(21)
Cd(2)–S(4)–P(4)	100.3(4)	S(4)–P(4)–O(4)	116.2(10)	O(12)–C(22)–C(24)	106.9(24)	C(23)–C(22)–C(24)	92.2(22)

3.98 Å and the Cd(2) • • • Cd(1a) distance is 6.76 Å. The Cd–S and Cd–O distances which are in the ranges 2.447(7)–2.491(6) and 2.139(15)–2.175(17) Å respectively are normal though the Cd–S bond associated with the ligand which links the Cd_2L_3 units is marginally shorter than those within the units themselves. The P–S distances are in the range 1.960(11)–1.987(9) Å and are as expected for this anion. There is also the expected distinction between the two types of P–O bonds with those to the OPr^i groups being longer [1.590(13)–1.603(16) Å] than their P–O–Cd counterparts [1.412(18)–1.533(12) Å]

We have made several efforts to determine the structures of complexes **1** and **2** but crystals of the zinc complex were always severely twinned. Powder diffraction studies show **1** and **2** to be isomorphous. A limited single-crystal study (*R ca.* 0.15) of the cobalt complex using a partially twinned crystal showed it to have a polymeric structure that is isostructural with that of the cadmium compound though the crystals are not isomorphous. The limited precision of the structure precludes any detailed discussion although the angular distortions at the metal and co-ordinating oxygen atoms observed in complex **3**

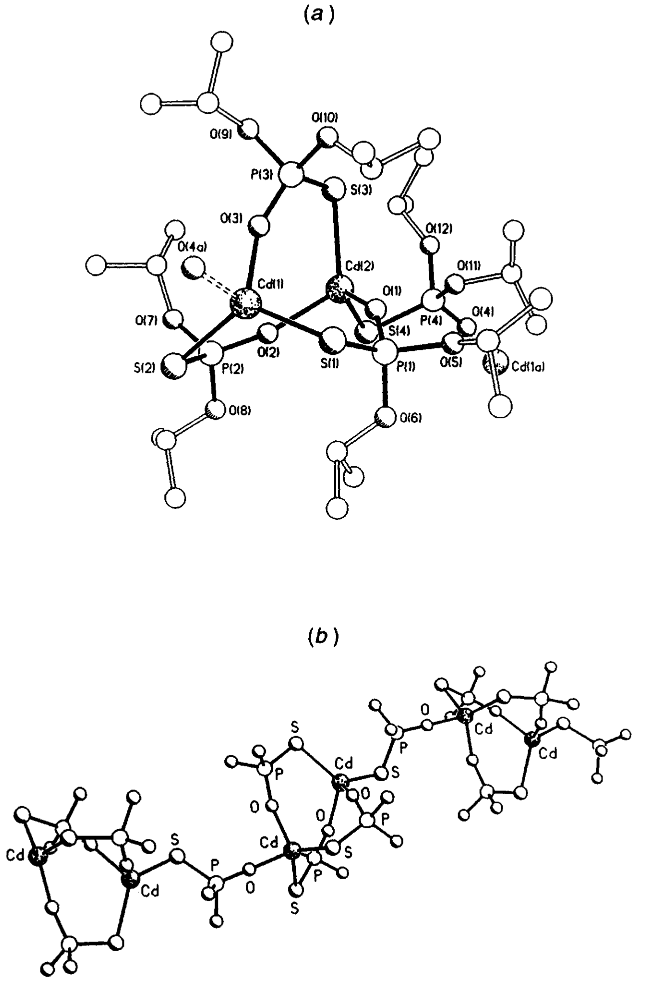


Fig. 1 The crystal structure of complex **3**; (*a*) a single Cd_2L_3 cage showing the numbering scheme and (*b*) part of one of the polymeric chains

are also present in **1** and **2**. The triply bridging polymeric structure observed here contrasts with the bimetallic structures in which each metal atom is bound to one chelating and two bridging monothiophosphate ligands which have been previously reported for zinc dialkyl dithiophosphates,[16] cobalt dialkylthiophosphinates[17] and phosphinates.[18]

The polymeric nature of the complexes was not evident in the mass spectra of complexes **1** or **2** which gave rather poor spectra under all conditions employed. In complex **3** the positive FAB mass spectrum contained peaks due to both $[Cd_2L_3]^+$ and larger fragments such as $[Cd_3L_5]^+$. The cadmium complex gives rise to a single peak in its ^{31}P NMR spectrum, revealing little about the structure. The ^{31}P NMR spectrum of the zinc complex in $CDCl_3$, however, consists of two peaks at δ 44.5 and 42.2 with an intensity ratio of 1 : 3. This is true over a wide range of concentrations, although at higher concentrations the peaks are often broad, with that at δ 44.5 appearing as only a shoulder on the larger peak, but still clearly discernible. Zinc complexes of the dialkyl dithiophosphates and the dialkyl monothiophosphinates usually give rise to only a single peak in their solution ^{31}P NMR spectra despite the apparent inequivalence of the ligands seen in their solid-state structures, such as distinct bridging and chelating ligands. The NMR equivalence of the phosphorus centres is generally ascribed to fluxional behaviour in solution and cooling the samples can in some cases allow resolution of the peaks. The polymeric structure of the zinc diisopropyl monothiophosphate **1** appears to persist in solution in non-co-ordinating solvents even at relatively low concentrations. The addition of a co-ordinating solvent or another competing ligand appears to break up the structure; in EtOD or thf the spectrum contains only one peak at δ 44.6 or 44.8 respectively. Addition of triethylamine to the $CDCl_3$ solution initially gives a product which gives rise to a peak at δ 46.3. If more of the amine is added a second peak at δ 55.9 appears which grows at the expense of that at δ 46.3. The final product, after the addition of an excess of the amine gives rise to only one peak at δ 55.1. This sequence is shown in Fig. 2.

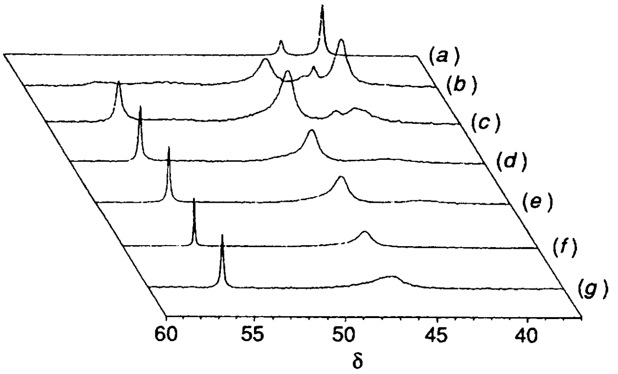


Fig. 2 The ^{31}P NMR spectra ($CDCl_3$) of (*a*) $Zn[O(S)P(OPr^i)_2]_2$ **1**, (*b*) **1** + $\frac{1}{4}$NEt$_3$, (*c*) **1** + $\frac{1}{2}$NEt$_3$, (*d*) **1** + $\frac{3}{4}$NEt$_3$, (*e*) **1** + NEt$_3$, (*f*) **1** + 2NEt$_3$, (*g*) **1** + 4NEt$_3$

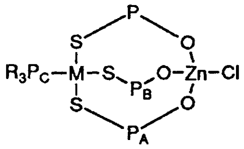
The peak at δ 44.5 in the original sample of $Zn[O(S)P(OPr^i)_2]_2$ does not appear to be due to an impurity, although there are possible candidates such as a basic form of the monothiophosphate. If it were an impurity its relative concentration with respect to the main product should vary depending on the conditions of preparation and with purification and in this case the ratio of the peaks remains constant in all samples. The two peaks in the spectrum of the zinc diisopropyl monothiophosphate must therefore be due to the singly bonded and triply bridging thiophosphate ligands. In the more co-ordinating alcohol solvent the ethanol co-ordinates to the metal breaking up the polymer. This change can also be seen clearly with the cobalt complex. Solutions of $Co[O(S)P(OPr^i)_2]_2$ in chlorinated and aromatic solvents are blue, implying tetrahedral co-ordination about the cobalt atoms, but in ethanol the complex turns pink as the co-ordination around the metal becomes octahedral. Earlier experiments[19–21] on zinc dialkyl dithiophosphates have shown that the addition of an amine gradually reduces the co-ordination of the dithiophosphates; first they become monodentate and if enough base is added they are eventually completely displaced. A similar displacement appears to occur here, the first effect of the base being to co-ordinate to the metal, breaking up the polymer, in the same way that ethanol and thf do. Once the amine is present in a greater concentration it begins to displace the thiophosphate ligands. Whether any of the peaks seen are specifically due to monodentate monothiophosphate is unclear, but the chemical shift of the final product, after addition of excess amine is very close to the shifts of both sodium and ammonium monothiophosphates and can be reasonably reliably assigned as unco-ordinated monothiophosphate.

As can be seen from Table 4 the infrared spectra of the monothiophosphates do not provide a very reliable structural guide. There are, however, some common features. In the sodium salts and the ammonium salt the ν(PS) band appears between 8 and 12 cm^{-1} below the value seen in the free acid. The drop in frequency is presumably attributable to the effects of delocalisation after deprotonation and co-ordination to the metal. The ν(PS) band in $Ni[O(S)P(OPr^i)_2]_2$ comes at about the same position as in the corresponding sodium salts, but for the three polymeric complexes (zinc, cobalt and cadmium) the band is split. The frequency of the ν(PO) band in the sodium salts of $PS(OPr^i)_2(OH)$, $PS(OMe)_2(OH)$ and $PS(OPh)_2(OH)$

Table 4 The ^{31}P NMR and infrared data (cm^{-1}) of the monothiophosphate complexes

$[M\{OP(S)(OR)_2\}_x]$					
M	R	$\delta(^{31}P)$	ν(PS)	ν(PO)	ν(P–O–C)
H	Pr^i	57.5	621	1180, 1144	1000
Na	Pr^i	54.7	613	1108	983
NH_4	Pr^i	53.8	609	1111	979
Zn	Pr^i	42.2, 44.5	639, 615	1179, 1160	987
Co	Pr^i	—	642, 616	1177, 1145	988
Cd	Pr^i	47.2	631, 595	1178	984
Ni	Pr^i	49.1	607	1181	988

Table 5 Infrared (cm^{-1}) and NMR data for complexes **6** (M = Pd) and **7** (M = Pt)



	$\delta(P_A)$ [$^2J(P_A$–Pt)/Hz]	$\delta(P_B)$ [$^2J(P_B$–Pt)/Hz]	$\delta(P_C)$ [$^1J(P_C$–Pt)/Hz]	ν(PS)	ν(PO)	ν(P–O–C)
6 (M = Pd)	39.9	39.9	5.8	645, 615	1179, 1155	995, 976
7 (M = Pt)	34.5 [84.7]	44.4 [91.4]	−10.8 [3414.7]	644, 614	1179, 1158	996, 977

shifts to about 70 cm^{-1} below the frequency observed in the free ligand.[19] In all of the transition-metal complexes this band is seen at almost the same position as in the free ligand regardless of the structure of the complex. The absorptions due to ν(PO) in the P–O–C groups show a distinct drop in frequency (12–21 cm^{-1}) upon the deprotonation of $PS(OPr^i)_2(OH)$, but beyond that show little sensitivity to the type of complex formed.

We have previously shown[10] that the reaction between $[PtCl_2(PMe_2Ph)_2]$ and $Zn[O(S)P(OPr^i)_2]_2$ **1** produces the bimetallic species **5**. The related reactions between **1** and $[PPh_4][PtCl_3(PMe_2Ph)]$ or $[PPh_4][PdCl_3(PMe_2Ph)]$ also give bimetallic products. Both reactions proceed very quickly at room temperature according to equation (6) in each case

$$2[PPh_4][MCl_3(PMe_2Ph)] + 3Zn[O(S)P(OPr^i)_2]_2 \longrightarrow 2[PPh_4]Cl + ZnCl_2 + 2[(PMe_2Ph)M\{O(S)P(OPr^i)_2\}_3ZnCl] \quad (6)$$

producing a single product in quantitative yield (M = Pt **6** or Pd **7**). The ^{31}P NMR spectrum of the platinum complex (Table 5) indicates that the three monthiophosphate ligands and the phosphine are all co-ordinated to platinum. The spectrum consists of three main peaks in the intensity ratio 1:2:1. The phosphorus–platinum coupling constants of 84.7 and 91.4 Hz for the first two peaks are typical of $^2J(^{31}P–^{195}Pt)$ interactions while the $^1J(^{31}P–^{195}Pt)$ coupling constant of 3414.7 Hz due to the phosphine is typical for a phosphorus *trans* to a sulfur. The coupling between the phosphine and the thiophosphates was of too small a magnitude to be resolved. The ^{31}P NMR spectrum of the palladium complex contains only two peaks, the two monothiophosphate peaks being reduced to a single broad line presumably due to an exchange in solution which renders all the ligands equivalent.

The ^{195}Pt NMR spectrum of the platinum complex was also recorded, because of the similarity between the two $^2J(^{31}P–^{195}Pt)$ coupling constants instead of seeing a doublet of double doublets the spectrum appears as a doublet of quartets centred at δ −6136.

The infrared spectra of the two bimetallic complexes are indistinguishable. The ν(PS) absorption is clearly split into two, but appears at about the same place as for the zinc complex. The ν(P–O–C) peak is also split, the absorptions coming either side of the value of 987 cm^{-1} recorded for $Zn[O(S)P(OPr^i)_2]_2$. The ν(PO) absorption is of much lower intensity than in any of the other monothiophosphate complexes.

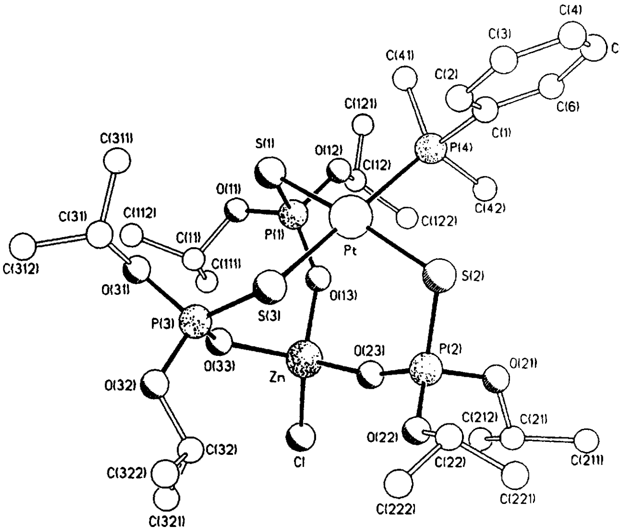


Fig. 3 The crystal structure of complex **7**; the palladium complex **6** is isomorphous

The structures of complexes **6** and **7** (Tables 6–8, Fig. 3) contain tetrahedral zinc centres linked to a square planar metal atom *via* three O–P–S bridges forming a cage which is topologically similar to that in complexes **1**–**3** with a polymeric structure being inhibited by the presence of the PMe_2Ph ligand. As expected the zinc binds to the 'hard' oxygen atoms and the Pt or Pd atom co-ordinates to the soft sulfurs of the thiophosphate ligands.

For complex **7** the geometry at zinc is essentially tetrahedral with only one significant departure for O(13)–Zn–O(33) [99.7(2)°] the remaining angles being in the range 110.0(2)–112.7(2)°. The square-planar geometry at platinum shows a small tetrahedral distortion with deviations of up to 0.18 Å from the S(1)–S(2)–S(3)–P(4) mean plane with S(3) and P(4) lying below and S(1) and S(2) above the plane (a similar effect is seen in the palladium structure the maximum deviation being 0.25 Å).

Table 6 Selected bond lengths (Å) and angles (°) for complexes **6** (M = Pd) and **7** (M = Pt)

	7	**6**		**7**	**6**
M–S(1)	2.333(2)	2.337(2)	Zn–Cl	2.191(2)	2.187(2)
M–S(2)	2.338(2)	2.344(2)	S(1)–P(1)	2.013(3)	2.007(3)
M–S(3)	2.402(2)	2.416(2)	S(2)–P(2)	2.026(3)	2.014(3)
M–P(4)	2.241(2)	2.260(2)	S(3)–P(3)	2.004(3)	1.995(3)
Zn–O(13)	1.963(4)	1.962(4)	P(1)–O(13)	1.488(5)	1.494(5)
Zn–O(23)	1.940(5)	1.945(5)	P(2)–O(23)	1.475(5)	1.463(5)
Zn–O(33)	1.966(5)	1.959(4)	P(3)–O(33)	1.492(5)	1.491(5)
S(1)–M–S(2)	173.3(1)	173.1(1)	O(13)–Zn–O(23)	111.4(2)	108.4(2)
S(1)–M–S(3)	94.0(1)	94.9(1)	O(13)–Zn–O(33)	99.7(2)	101.1(2)
S(1)–M–P(4)	94.3(1)	93.3(1)	O(23)–Zn–O(33)	110.7(2)	110.5(2)
S(3)–M–P(4)	166.9(1)	166.3(1)	O(13)–Zn–Cl	112.7(2)	113.1(3)
S(1)–P(1)–O(13)	116.7(2)	116.3(2)	O(23)–Zn–Cl	110.0(2)	111.0(2)
S(2)–P(2)–O(23)	118.5(2)	118.3(2)	O(33)–Zn–Cl	111.9(1)	112.3(1)
S(3)–P(3)–O(33)	116.0(2)	116.0(2)	Zn–O(13)–P(1)	137.5(3)	137.3(3)
O(11)–P(1)–O(12)	102.0(3)	102.0(3)	Zn–O(23)–P(2)	166.3(2)	168.8(3)
O(21)–P(3)–O(22)	107.7(3)	110.9(3)	Zn–O(33)–P(3)	132.1(3)	133.2(3)
O(31)–P(3)–O(32)	101.2(3)	107.4(3)			

Table 7 Atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	1209(1)	2424(1)	2848(1)	C(3)	−1656(7)	3929(5)	3264(5)
Zn	3843(1)	1686(1)	3057(1)	C(4)	−1673(8)	4569(5)	3117(6)
S(1)	1191(1)	1767(1)	1657(1)	C(5)	−919(9)	4842(4)	2684(5)
S(2)	1440(2)	3109(1)	4008(1)	C(6)	−69(7)	4485(4)	2397(5)
S(3)	1110(2)	1549(1)	3837(1)	C(11)	3483(7)	735(4)	976(5)
P(1)	2659(2)	1893(1)	1259(1)	C(111)	4561(7)	769(5)	598(6)
P(2)	2891(2)	2814(1)	4370(1)	C(112)	2866(9)	170(4)	725(7)
P(3)	1917(2)	784(1)	3466(1)	C(12)	3517(6)	2631(4)	84(4)
P(4)	964(2)	3329(1)	2086(1)	C(121)	3085(7)	2878(5)	−711(5)
O(11)	2921(4)	1306(2)	686(3)	C(122)	4201(9)	3081(7)	532(6)
O(12)	2616(3)	2456(2)	613(3)	C(21)	4596(7)	3495(4)	4696(7)
O(13)	3488(3)	2009(2)	1925(3)	C(211)	4792(8)	4178(4)	4910(6)
O(21)	3541(4)	3461(2)	4353(3)	C(212)	5369(7)	3249(4)	4092(7)
O(22)	2899(4)	2565(3)	5293(3)	C(22)	2214(7)	2805(5)	5954(5)
O(23)	3395(4)	2317(2)	3874(3)	C(221)	2710(12)	3289(8)	6408(9)
O(31)	1286(4)	349(2)	2826(3)	C(222)	2033(12)	2256(7)	6517(8)
O(32)	2038(4)	322(2)	4239(3)	C(31)	216(6)	143(4)	2995(5)
O(33)	2958(3)	919(2)	3097(3)	C(311)	−529(8)	455(5)	2406(7)
Cl	5513(2)	1463(1)	3239(2)	C(312)	183(8)	−557(5)	2916(9)
C(41)	494(6)	3260(4)	1010(4)	C(32)	2669(8)	523(5)	4963(5)
C(42)	2135(6)	3806(4)	2041(5)	C(321)	3605(10)	202(9)	5033(8)
C(1)	−40(6)	3829(3)	2542(4)	C(322)	2092(10)	322(7)	5636(8)
C(2)	−839(6)	3558(4)	2982(5)				

The angles at platinum are in the ranges 86.2(1)–94.3(1) and 166.9(1)–173.3(1)°. The geometry at S(1) and S(2) is normal [Pt–S–P angles of 101.1(1) and 98.8(1)° respectively] whereas the Pt–S(3)–P(3) angle is enlarged to 112.6(1)°. The Zn–O–P angles are wide ranging [Zn–O(33)–P(3) 132.1(3), Zn–O(13)–P(1) 137.5(3) and Zn–O(23)–P(2) 166.3(3)°; the Zn–O(23)–P(2) angle in complex **6** is 168.8(3)°]. The enlarged angle at O(23) is accompanied by an essentially coplanar geometry for the Zn–O(23)–P(2)–S(2)–Pt or Pd linkage compared with the twisted geometries observed for the other two bridging linkages. The intracage Pt • • • Zn distance is 3.17 Å (Pd • • • Zn in **6** 3.70 Å). The Zn–O and Zn–Cl distances are normal as are the Pt–S and Pt–P distances, there being a small lengthening of the Pt–S distance for S(3) *trans* to phosphorus compared to the other Pt–S distances [2.402(2) *cf.* 2.333(2) and 2.338(2) Å]. The P–O and P–S distances are comparable with those of complex **3** with, as expected, the P–OPr^i bonds being longer than those of P–OM.

Addition of pyridine (py) to [(PMe$_2$Ph)Pt{O(S)P(OPr^i)$_2$}$_3$ZnCl] results in the formation of a new complex containing monothiophosphate ligands and a phosphine bound to platinum. The ^{31}P NMR spectrum shows a product in which the ratio of monothiophosphate to phosphine is 2 : 1, but the monothiophosphates are both equivalent. Concentration of this solution only gives an oily product and the only product that could be extracted cleanly from the solution was [ZnCl$_2$(py)$_2$]. The same platinum complex can also be synthesised from the reaction of ammonium diisopropyl monothiophosphate with pyridine and [PPh$_4$][Pt(PMe$_2$Ph)Cl$_3$]. These results suggest that the platinum complex formed is [Pt{O(S)P(OPr^i)$_2$}$_2$(PMe$_2$Ph)(py)] according to equation (7).

$$[(\mathrm{PMe_2Ph})\mathrm{Pt}\{\mathrm{O(S)P(OPr^i)_2}\}_3\mathrm{ZnCl}] + 3\,\mathrm{py} \longrightarrow [\mathrm{Pt}\{\mathrm{O(S)P(OPr^i)_2}\}_2(\mathrm{PMe_2Ph})(\mathrm{py})] + [\mathrm{ZnCl_2(py)_2}] + [\mathrm{Zn}\{\mathrm{O(S)P(OPr^i)_2}\}_2] \qquad (7)$$

This would explain the formation of [ZnCl$_2$(py)$_2$] and perhaps the difficulty in recovering the other products cleanly. The [Zn{O(S)P(OPr^i)$_2$}$_2$] gives a broad peak in the NMR spectrum of the product mixture because of the presence of the pyridine, the effect being similar to that seen with small amounts of triethylamine as discussed above.

The bimetallic compounds **5**–**7** represent an interesting class of compounds containing both hard and soft metals; further work in this area is in progress.

Table 8 Atomic coordinates (× 10^4) for complex **7**

Atom	*x*	*y*	*z*
Pt	1198(1)	2423(1)	2854(1)
Zn	3845(1)	1688(1)	3074(1)
S(1)	1186(1)	1759(1)	1674(1)
S(2)	1426(2)	3080(1)	4035(1)
S(3)	1108(2)	1552(1)	3835(1)
P(1)	2661(2)	1883(1)	1272(1)
P(2)	2897(2)	2803(1)	4402(1)
P(3)	1920(2)	786(1)	3468(1)
P(4)	973(2)	3321(1)	2101(1)
O(11)	2911(4)	1299(2)	696(3)
O(12)	2615(4)	2448(2)	622(3)
O(13)	3498(3)	1993(2)	1931(3)
O(21)	3537(4)	3446(2)	4371(3)
O(22)	2905(4)	2574(2)	5335(3)
O(23)	3412(4)	2295(2)	3919(3)
O(31)	1290(4)	345(2)	2832(3)
O(32)	2036(4)	335(2)	4255(3)
O(33)	2962(3)	917(2)	3094(3)
Cl	5520(2)	1462(1)	3259(2)
C(41)	505(6)	3256(3)	1023(4)
C(42)	2152(6)	3798(4)	2067(5)
C(1)	−38(6)	3833(3)	2539(4)
C(2)	−838(6)	3565(4)	2991(5)
C(3)	−1648(6)	3950(5)	3283(5)
C(4)	−1646(8)	4585(5)	3118(5)
C(5)	−898(8)	4849(4)	2674(5)
C(6)	−57(7)	4484(3)	2394(5)
C(11)	3487(7)	738(4)	985(5)
C(111)	4562(7)	780(5)	603(6)
C(112)	2889(9)	165(4)	736(6)
C(12)	3508(6)	2618(4)	97(5)
C(121)	3074(8)	2842(5)	−720(5)
C(122)	4198(9)	3080(7)	537(6)
C(21)	4591(7)	3496(4)	4700(6)
C(211)	4766(8)	4185(4)	4913(7)
C(212)	5368(8)	3243(4)	4106(7)
C(22)	2227(7)	2814(5)	5987(5)
C(221)	2736(11)	3298(8)	6431(8)
C(222)	2071(12)	2291(7)	6583(8)
C(31)	215(6)	144(4)	3005(5)
C(311)	−521(8)	444(5)	2422(7)
C(312)	189(8)	−561(5)	2931(9)
C(32)	2719(8)	530(5)	4971(5)
C(321)	3634(10)	175(9)	5021(8)
C(322)	2106(10)	349(6)	5659(8)

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