Journal of Organometallic Chemistry, 193 (1980) 1—12

X-RAY CRYSTAL STRUCTURE DETERMINATION OF BIS(TRIPHENYLBENZYLPHOSPHONIUM) TETRACHLOROCADMATE DICHLOROETHANE SOLVATE

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(Received January 9th, 1980)

Summary

The molecular and crystal structure of the title compound has been determined from X-ray diffractometer data. The structure was solved by direct and Fourier methods and refined by least-squares techniques to $R = 0.063$ for 2246 independent reflections. Crystals are monoclinic, space group $P2_1/c$, with four $[CdCl_4]^{2-} \cdot 2[(C_6H_5)_3PCH_2C_6H_5]^+ \cdot 2\ Cl_2C_2H_4$ formula units in a unit-cell of dimensions *a* 14.73(2), *b* 24.88(3), *c* 16.37(2) Å, β 112.61(10)°.

The tetrachlorocadmate(II) anion shows a quasi-perfect tetrahedral symmetry and is surrounded by two dichloroethane solvent molecules. The benzyltriphenylphosphonium cations adopt quasi-perfect tetrahedral symmetry around the P atoms with the P—C(Phen) bonds in slightly distorted staggered conformations (*gauche*—, *gauche*+, and *trans*) with respect to the C(Phen)—CH$_2$ bond of the benzyl groups. The bond lengths and angles of the ions are in excellent agreement with literature data. The parameters of the dichloroethane molecules are rather poorly defined as the crystal loses the solvent even at room temperature and atmospheric pressure. The Cl—C bonds of the two $ClCH_2CH_2Cl$ molecules are nearly in the *gauche* conformation. The interatomic distances between the ions correspond to the usual Van der Waals distances.

Introduction

Complexes with the empirical formula R_3PCdX_2 ($R = C_6H_5$, C_6H_{11}, alkyl; X = Cl, Br), resulting from the reaction of R_3P with anhydrous $CdCl_2$, have been described as non-ionic 1 : 1 complexes with a dimeric tetrahedral structure (C_{2h} skeletal symmetry) [1—3]. Metal—phosphorous bonding has been reported for the cadmium(II) complexes $(R_3P)_2CdX_2$ [4—6]. By slight modification of

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* Deceased.

the reaction conditions, interaction of $CdCl_2$ or $CdBr_2$ with triphenylphosphine, $C_6H_5CH_2Cl$ and/or $C_6H_5CH_2Br$, leads to products with a stoichiometry essentially different from that of the complexes described above. It was therefore of interest to establish the nature of the species present, in particular with reference to metal—phosphorus bonding as an alternative to an ionic structure involving the triphenylbenzylphosphonium system. This paper describes the crystal and molecular structure of the clathrate $[CdCl_4]^{2-} \cdot 2[(C_6H_5)_3PCH_2C_6H_5]^{+}$ $2\ Cl_2C_2H_4$ (I).

Experimental

Bis(triphenylbenzylphosphonium) tetrachlorocadmate(I), crystallized from a mixture of $ClCH_2CH_2Cl$ and $Cl_2C{=}CCl_2$, retains two dichloroethane molecules per independent unit. The clathrate obtained loses solvent molecules even at room temperature and atmospheric pressure. Thermogravimetric analysis showed that the solvent is totally eliminated by the crystals at a temperature of about 72° C, when a rearrangement of the structure occurs (cfr. b.p. $ClCH_2CH_2Cl$, 83.5° C).

A colourless crystal of I was firmly mounted in a Lindemann glass capillary tube filled with dry nitrogen and flame sealed. Preliminary space-group and unit-cell dimensions were obtained from Weissenberg photographs. A crystal, essentially a parallelepided with dimensions of 0.4 × 0.5 × 0.6 mm was then mounted on a Picker FACS1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. The orientation matrix and cell dimensions were obtained from a least-squares fit of χ, φ, ω, and 2θ values from 12 independent reflections.

Crystal data

$C_{50}H_{44}P_2 \cdot CdCl_4 \cdot 2\ C_2H_4Cl_2$: Mol. wt. 1159.03; monoclinic, a 14.73(2), b 24.88(3), c 16.37(2) Å, β 112.61(10)°; U 5538.23 Å^3; D_0 1.42, D_c 1.394 g cm^{-3}; $Z = 4$, m.p. 210° C. Space group $P2_1/c$ from systematic absences ($h0l$) for l odd and ($0k0$) for k odd, μ(Mo-K_α) 8.7 cm^{-1}.

Intensity data were collected by use of zirconium filtered Mo-K_α radiation (λ 0.71069 Å) with $2\theta \leqslant 35°$. The moving crystal-moving counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2.0—2.5°, in order to allow for the greater separation of the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks at increasing 2θ values.

Background counts of 10 s were measured at each end of a 2θ scan. Three standard reflections, measured after every 50 reflections, showed that the crystal was slowly decomposing. At the end of the data collection the decrease of the intensities of the standard reflections was about 25%. In order to take this effect into account the intensities of all reflections were scaled to the beginning of the data collection on the basis of the intensities of the monitoring reflections. 3496 independent reflections were measured of which 2246 were considered observed and had $I \geqslant 2.50\sigma$ ($\sigma = [N_s + (t_s/t_b)^2N_b]^{1/2}$, where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent in measuring the N_b background counts). An arbitrary intensity equal to half the observable limit was assigned to the non-significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced ($\mu_R = 0.26$).

Determination and refinement of the structure

The structure was solved by direct methods using the 1974 version of the MULTAN program written by Main, Woolfson, Lessinger, Germain, and Declercq [7]. The observed structure factors were automatically converted by the program into normalized structure factor amplitudes $|E|$'s. All $|E| > 1.39$ (600 reflections) were introduced into the calculations and a further 50 reflections with very low $|E|$ value were fed into the program in order to define also the ψ_0 figure of merit. The number of phase relationships found was 25872 and 4990 were saved. The starting set, automatically chosen by the program, is reported in Table 1. Eight solutions were obtained according to the values (2π or π) of the phase angles A, B, and C.

The tangent formula results (Table 1) showed that solutions 3 and 4 have the same values for all the figures of merit. The corresponding phase angles A, B and C were all 2π for solution 3, and π, 2π and 2π for solution 4. The E-maps of both solutions were determined and the Fourier peaks were practically coincident for both solutions. From the E-maps it was possible to define the positional parameters of the cadmium, chlorine and phosphorous atoms of the independent unit of I. The coordinates of the carbon atoms and of the two $Cl_2C_2H_4$ solvent molecules were obtained by successive Fourier maps and on the basis of stereochemical considerations. The positional and the isotropic thermal parameters of the non-hydrogen atoms of the molecule were refined by several cycles of block-diagonal least-squares using Immirzi's program [8]. Atomic scattering factors were calculated from the expression in ref. 9

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TABLE 1

TANGENT FORMULA RESULTS

a) Tangent formula input

h	*k*	*l*	$\|E\|$	Phase angle	
−3	3	8	3.40	180°	Origin-fixing reflexions
−7	4	2	3.02	360°	
−1	6	3	2.23	180°	
−5	9	11	2.96	A	
−12	2	3	2.84	B	
0	2	3	2.66	C	

b) Tangent formula output

Numset	ABS FOM	ψ_0	Resid	Combined FOM
1	1.103	3106	36.85	1.190
2	1.102	3106	36.84	1.191
3	1.213	3142	29.07	2.000
4	1.213	3142	29.07	2.000
5	0.876	2303	43.91	0.977
6	0.877	2284	43.92	1.004
7	0.932	2774	42.98	0.658
8	0.932	2774	43.03	0.656

TABLE 2

FINAL FRACTIONAL COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*
Cd	−0.00261(9)	0.61762(5)	0.22583(7)
Cl(1)	0.0582(3)	0.5657(2)	0.1307(3)
Cl(2)	0.0701(4)	0.7070(2)	0.2501(4)
Cl(3)	−0.1802(4)	0.6268(3)	0.1519(3)
Cl(4)	0.0454(4)	0.5671(2)	0.3649(3)
P(1)	−0.0846(3)	0.3918(2)	0.3590(3)
P(2)	−0.2481(3)	0.5972(2)	0.8616(3)
C(1)	−0.1033(11)	0.3930(6)	0.2433(9)
C(2)	−0.0678(12)	0.4380(6)	0.2143(10)
C(3)	−0.0757(13)	0.4390(7)	0.1268(10)
C(4)	−0.1117(13)	0.3957(6)	0.0725(10)
C(5)	−0.1487(17)	0.3502(8)	0.1027(13)
C(6)	−0.1370(13)	0.3503(7)	0.1914(10)
C(7)	0.0373(10)	0.3667(6)	0.4176(8)
C(8)	0.0990(13)	0.3948(8)	0.4917(12)
C(9)	0.1956(13)	0.3747(8)	0.5372(11)
C(10)	0.2313(14)	0.3297(8)	0.5094(13)
C(11)	0.1658(12)	0.3044(8)	0.4375(12)
C(12)	0.0717(12)	0.3224(7)	0.3914(10)
C(13)	−0.1711(10)	0.3462(6)	0.3792(8)
C(14)	−0.2597(13)	0.3388(8)	0.3143(11)
C(15)	−0.3250(14)	0.3079(10)	0.3396(13)
C(16)	−0.3002(17)	0.2868(10)	0.4228(14)
C(17)	−0.2142(16)	0.2983(9)	0.4805(14)
C(18)	−0.1414(13)	0.3267(7)	0.4626(11)
C(19)	−0.1014(12)	0.4569(6)	0.3995(9)
C(20)	−0.2039(10)	0.4781(6)	0.3584(9)
C(21)	−0.2379(12)	0.5092(7)	0.2853(10)
C(22)	−0.3266(15)	0.5283(9)	0.2497(12)
C(23)	−0.3979(12)	0.5154(8)	0.2861(12)
C(24)	−0.3672(14)	0.4846(8)	0.3602(13)
C(25)	−0.2706(13)	0.4654(7)	0.3954(11)
C(26)	−0.1915(10)	0.5448(7)	0.9383(10)
C(27)	−0.2663(11)	0.5041(6)	0.9436(9)
C(28)	−0.3036(12)	0.5104(8)	1.0088(11)
C(29)	−0.3721(16)	0.4744(9)	1.0117(12)
C(30)	−0.4048(13)	0.4334(9)	0.9488(13)
C(31)	−0.3675(15)	0.4257(8)	0.8881(12)
C(32)	−0.2974(12)	0.4635(7)	0.8829(10)
C(33)	−0.2857(11)	0.5756(7)	0.7514(10)
C(34)	−0.3668(13)	0.5952(7)	0.6870(9)
C(35)	−0.3855(16)	0.5829(9)	0.5998(12)
C(36)	−0.3189(17)	0.5506(8)	0.5783(12)
C(37)	−0.2414(15)	0.5305(8)	0.6387(12)
C(38)	−0.2165(13)	0.5416(7)	0.7277(10)
C(39)	−0.3543(11)	0.6236(6)	0.8745(9)
C(40)	−0.3525(11)	0.6712(7)	0.9111(11)
C(41)	−0.4340(14)	0.6919(7)	0.9213(11)
C(42)	−0.5181(15)	0.6606(7)	0.8997(13)
C(43)	−0.5218(13)	0.6116(8)	0.8639(13)
C(44)	−0.4353(12)	0.5916(8)	0.8507(11)
C(45)	−0.1627(11)	0.6499(6)	0.8810(9)
C(46)	−0.1013(12)	0.6657(7)	0.9638(10)
C(47)	−0.0403(15)	0.7107(9)	0.9722(12)
C(48)	−0.0428(13)	0.7364(8)	0.8993(12)
C(49)	−0.1046(16)	0.7212(9)	0.8138(13)
C(50)	−0.1644(13)	0.6801(7)	0.8027(12)

TABLE 2 (continued)

Atom	*x/a*	*y/b*	*z/c*
Cl(5)	0.4177(7)	0.2682(3)	0.3734(6)
Cl(6)	0.4446(6)	0.1798(4)	0.2284(5)
Cl(7)	0.4117(6)	0.5771(4)	0.3672(6)
Cl(8)	0.3814(9)	0.7062(5)	0.3910(9)
C(51)	0.3587(21)	0.2092(11)	0.3356(20)
C(52)	0.3501(24)	0.1856(15)	0.2673(25)
C(53)	0.3041(20)	0.6137(13)	0.3399(24)
C(54)	0.3119(20)	0.6651(14)	0.2994(21)
H(2)	−0.035	0.472	0.260
H(3)	−0.053	0.475	0.100
H(4)	−0.111	0.395	0.005
H(5)	−0.188	0.317	0.057
H(6)	−0.155	0.315	0.221
H(8)	0.074	0.432	0.513
H(9)	0.243	0.397	0.596
H(10)	0.308	0.314	0.544
H(11)	0.191	0.268	0.414
H(12)	0.022	0.299	0.334
H(14)	−0.280	0.355	0.246
H(15)	−0.400	0.301	0.291
H(16)	−0.353	0.263	0.442
H(17)	−0.195	0.286	0.551
H(18)	−0.065	0.331	0.511
H(191)	−0.077	0.455	0.471
H(192)	−0.051	0.486	0.385
H(21)	−0.185	0.519	0.255
H(22)	−0.349	0.553	0.191
H(23)	−0.476	0.529	0.258
H(24)	−0.417	0.476	0.393
H(25)	−0.249	0.439	0.454
H(261)	−0.138	0.524	0.918
H(262)	−0.153	0.562	1.004
H(28)	−0.279	0.545	1.056
H(29)	−0.402	0.478	1.064
H(30)	−0.463	0.406	0.951
H(31)	−0.393	0.391	0.840
H(32)	−0.267	0.460	0.831
H(34)	−0.418	0.621	0.704
H(35)	−0.454	0.694	0.546
H(36)	−0.332	0.544	0.508
H(37)	−0.196	0.503	0.617
H(38)	−0.148	0.527	0.779
H(40)	−0.283	0.594	0.935
H(41)	−0.434	0.733	0.946
H(42)	−0.582	0.679	0.910
H(43)	−0.590	0.586	0.848
H(44)	−0.435	0.551	0.820
H(46)	−0.101	0.643	1.022
H(47)	0.010	0.722	1.039
H(48)	0.006	0.772	0.909
H(49)	−0.101	0.742	0.756
H(50)	−0.223	0.664	0.821
H(511)	0.299	0.202	0.359
H(512)	0.292	0.227	0.255
H(521)	0.458	0.157	0.372
H(522)	0.349	0.131	0.290
H(531)	0.241	0.588	0.306
H(532)	0.296	0.623	0.405
H(541)	0.345	0.657	0.249
H(542)	0.235	0.680	0.257

TABLE 3

ANISOTROPIC THERMAL PARAMETERS (Å^2) IN THE FORM $\exp - 1/4(B_{11}a^{\star 2}h^2 + B_{22}b^{\star 2}k^2 + B_{33}c^{\star 2}l^2 + 2B_{12}a^{\star}b^{\star}hk + 2B_{13}a^{\star}c^{\star}hl + 2B_{23}b^{\star}c^{\star}kl)$. Standard deviations in parentheses. [a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd	5.74(7)	5.95(7)	3.85(6)	0.30(6)	2.34(5)	−0.23(5)
Cl(1)	6.89(26)	6.17(27)	4.60(22)	1.34(21)	3.22(20)	0.51(19)
Cl(2)	9.16(34)	5.38(28)	8.98(33)	0.67(24)	0.17(28)	−0.13(24)
Cl(3)	5.12(26)	13.46(45)	5.93(27)	1.04(27)	2.68(22)	−0.76(27)
Cl(4)	7.81(29)	8.99(33)	2.98(20)	−0.78(24)	2.58(20)	1.09(21)
P(1)	4.76(23)	4.45(24)	3.30(21)	−0.20(18)	1.68(18)	0.56(18)
P(2)	3.93(22)	6.10(28)	3.12(20)	0.08(19)	1.20(17)	−0.07(19)
C(1)	5.58(87)	4.77(90)	2.92(75)	0.12(70)	1.44(67)	0.55(64)
C(2)	5.98(92)	5.21(92)	4.01(81)	−0.54(74)	2.82(72)	0.10(71)
C(3)	8.26(115)	5.60(103)	4.59(89)	0.03(85)	2.47(84)	0.13(77)
C(4)	8.15(111)	4.75(98)	3.69(85)	2.27(81)	1.49(79)	1.76(70)
C(5)	12.47(160)	6.84(123)	6.73(114)	0.80(111)	3.87(111)	−2.75(99)
C(6)	8.23(115)	5.92(103)	4.40(89)	−1.44(87)	2.86(83)	−0.84(78)
C(7)	5.22(84)	5.44(90)	1.46(64)	0.31(70)	2.56(62)	1.11(60)
C(8)	6.50(100)	10.06(143)	5.81(104)	1.43(98)	2.60(88)	−1.34(95)
C(9)	6.14(104)	7.71(122)	5.51(100)	−0.44(89)	0.76(83)	0.32(87)
C(10)	7.47(118)	7.15(123)	8.79(125)	0.94(94)	3.66(100)	1.05(99)
C(11)	5.32(103)	7.74(121)	7.31(111)	2.96(89)	2.73(88)	0.49(92)
C(12)	6.68(107)	7.46(114)	4.16(86)	3.35(87)	2.18(79)	−1.10(79)
C(13)	4.38(81)	4.76(88)	1.92(66)	0.01(67)	0.04(59)	−0.57(63)
C(14)	6.54(108)	8.92(126)	5.01(93)	−2.26(92)	3.28(83)	−0.15(88)
C(15)	6.38(117)	14.72(189)	7.03(120)	0.69(120)	2.17(97)	−1.35(122)
C(16)	10.38(150)	12.96(182)	7.93(132)	−3.42(131)	2.56(115)	5.17(127)
C(17)	9.73(143)	11.19(162)	9.03(137)	−1.59(120)	5.08(116)	3.52(121)
C(18)	7.58(108)	5.27(100)	5.57(93)	0.90(82)	3.42(84)	2.49(79)
C(19)	6.96(98)	4.45(89)	2.73(74)	0.57(73)	2.23(69)	−1.45(63)
C(20)	4.68(84)	3.64(83)	4.91(84)	1.57(65)	2.81(70)	0.21(66)
C(21)	6.43(99)	5.88(101)	4.53(86)	1.25(82)	2.00(76)	0.37(76)
C(22)	9.65(137)	9.28(141)	6.23(112)	2.47(111)	2.61(100)	1.39(100)
C(23)	5.09(97)	8.76(129)	6.51(106)	0.47(90)	0.41(83)	−1.82(96)
C(24)	7.21(115)	8.70(135)	9.18(129)	−1.34(99)	4.57(103)	−3.16(106)
C(25)	8.27(119)	6.06(110)	5.81(100)	0.83(90)	2.32(90)	−2.72(84)
C(26)	2.46(75)	7.71(110)	4.14(82)	0.78(71)	0.83(64)	−0.01(75)
C(27)	4.66(82)	5.79(94)	3.41(76)	−0.03(71)	2.03(66)	0.49(68)
C(28)	5.56(97)	8.54(122)	6.06(100)	−0.37(88)	3.34(82)	−0.14(89)
C(29)	10.67(144)	11.49(158)	4.80(102)	−1.15(121)	3.20(101)	−1.77(101)
C(30)	6.30(111)	11.60(163)	6.98(115)	−2.57(106)	1.73(92)	2.61(107)
C(31)	9.11(128)	9.35(142)	6.60(110)	1.15(108)	4.14(99)	0.76(100)
C(32)	6.85(100)	6.47(105)	3.20(80)	−0.49(80)	2.04(74)	1.83(73)
C(33)	4.54(88)	5.77(101)	4.60(87)	−0.41(75)	0.43(71)	0.14(74)
C(34)	7.33(107)	8.32(120)	2.25(76)	−1.19(90)	1.65(75)	−0.61(76)
C(35)	9.63(136)	11.65(160)	4.00(97)	3.39(124)	−0.27(91)	2.81(103)
C(36)	14.00(177)	7.43(130)	6.29(114)	0.23(116)	4.86(120)	−1.45(95)
C(37)	10.51(138)	6.69(116)	6.05(104)	1.55(101)	3.77(100)	−0.41(88)
C(38)	6.66(103)	8.31(119)	3.76(86)	0.19(87)	2.39(77)	0.74(79)
C(39)	4.43(82)	6.75(104)	2.31(72)	−1.29(75)	0.68(64)	−0.30(68)
C(40)	3.97(83)	7.00(108)	5.84(94)	0.64(76)	2.38(73)	−1.44(80)
C(41)	8.58(121)	6.48(112)	5.96(100)	0.32(91)	3.94(91)	−0.91(86)
C(42)	10.70(141)	6.58(118)	8.35(121)	1.53(100)	7.00(113)	1.32(95)
C(43)	5.91(105)	9.47(136)	7.97(120)	1.18(94)	3.68(94)	2.08(100)
C(44)	4.52(90)	8.39(121)	6.39(102)	1.53(84)	2.23(80)	1.64(90)
C(45)	4.99(88)	5.41(93)	4.01(80)	−1.57(71)	2.78(69)	−1.27(71)
C(46)	5.82(95)	6.44(105)	4.97(88)	−1.84(78)	2.75(76)	−3.42(78)
C(47)	9.31(133)	9.67(141)	5.33(106)	−2.09(108)	2.64(96)	−3.69(98)
C(48)	6.28(107)	9.45(134)	7.59(116)	−3.16(96)	4.24(94)	−1.55(100)
C(49)	9.55(141)	11.57(166)	6.05(115)	−3.12(117)	3.21(105)	−0.86(105)
C(50)	6.59(104)	5.70(103)	7.24(106)	−2.04(83)	3.79(87)	−0.23(85)

TABLE 3 (continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(5)	18.15(74)	10.23(51)	14.15(61)	−3.33(47)	4.63(55)	−0.84(43)
Cl(6)	11.08(48)	20.81(81)	12.72(53)	4.03(52)	6.20(43)	2.04(53)
Cl(7)	11.99(54)	16.84(72)	13.27(58)	0.23(49)	2.85(45)	0.05(51)
Cl(8)	24.87(106)	18.68(89)	31.12(133)	−13.45(84)	20.53(107)	−12.96(92)
C(51)	15.32(210)	12.15(191)	19.68(252)	−7.41(167)	13.77(206)	−6.15(178)
C(52)	14.58(240)	20.91(313)	22.92(327)	−4.64(224)	12.71(245)	−7.42(263)
C(53)	8.61(160)	17.92(273)	21.75(315)	−2.01(165)	7.23(187)	3.06(225)
C(54)	10.35(182)	22.15(318)	17.11(250)	2.12(190)	8.27(182)	−1.64(226)

[a] All hydrogen atoms have an (arbitrarily imposed) isotropic temperature factor $B = 5$ Å^2.

using the values for the parameters given in ref. 10. The weighting scheme of ref. 11 was adopted:

$$1/w = A + B|F_0| + C|F_0|^2, \text{ where } A = 2\,F_0\,(\text{min}),\ B = 1, \text{ and } C = 2/F_0 \text{ max.}$$

When the conventional R factor had reached 0.110 for the 2246 non-zero reflections several more cycles of block-diagonal least-squares refinement were run, assuming anisotropic thermal parameters for all the non-hydrogen atoms of the molecule. The hydrogen atoms were introduced into the calculations but not refined, their coordinates being defined both on stereochemical grounds and on the basis of a three-dimensional difference Fourier map. The Δ F map did not show spurious peaks. The assumed B value for all the hydrogen atoms was 5.0 Å^2. The conventional R dropped to 0.063. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ.

Table 2 reports the final fractional coordinates and the corresponding standard deviations (in parentheses) of the atoms of the independent unit. Table 3 lists the anisotropic thermal parameters of the non-hydrogen atoms.

Calculated and observed structure amplitudes can be obtained by application to the authors.

Results and discussion

A view of the structure of a molecule of I is shown in Fig. 1 together with the atom labelling scheme and the thermal vibration ellipsoids. The packing of the molecules in the crystals is shown in Fig. 2. Both figures have been obtained by means of the ORTEP computing and drawing program [12]. The geometric parameters of the molecule with their estimated standard deviations are reported in Table 4.

The structure of I is built up by the juxtaposition at Van der Waals distances of well separated tetrachlorocadmate anions and phosphonium cations in the presence of solvent molecules.

The $[CdCl_4]^{2-}$ ion has a quasi-perfect tetrahedral symmetry with an average Cd—Cl bond length of 2.441(5) Å (range 2.433—2.455 Å) and an average of the Cl—Cd—Cl angles of 109.5(1)° (range 105.8—112.5°). The mean Cl–Cl distance (3.986 Å) is somewhat longer than the sum of the ionic radii (3.62 Å) of the

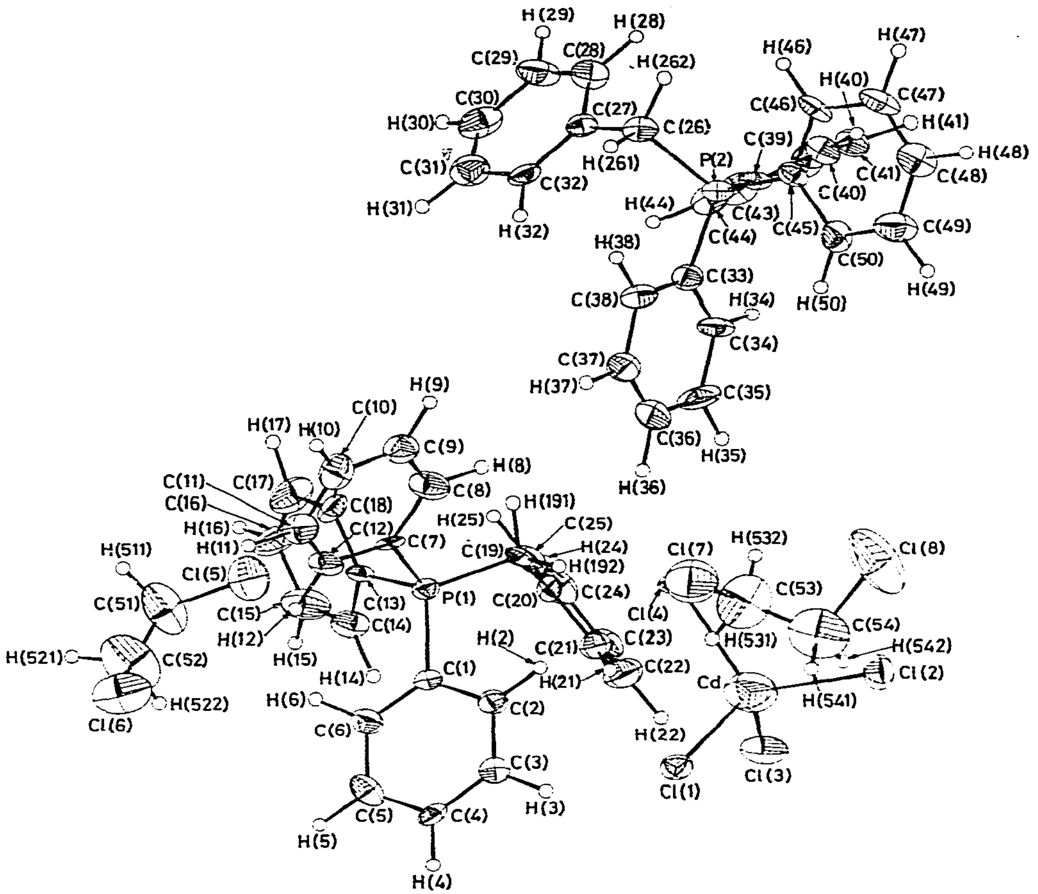

Fig. 1. View of the $[CdCl_4]^{2-} \cdot 2[(C_6H_5)_3PCH_2C_6H_5]^+ \cdot 2\,Cl_2C_2H_4$ clathrate indicating the atom labelling scheme and 30% probability thermal vibration ellipsoids.

chloride ions. Cadmium complexes in which the cadmium atom exists in a tetrahedral environment of chlorines are rare; examples are diquinolinium-tetrachlorocadmate (II) [13], thiaminium tetrachlorocadmate monohydrate (III) [14] and bis-(β-hydroxyethyltriphenylphosphonium)tetrachlorocadmate (IV) [15]. This work shows that the cadmium stereogeometry is essentially maintained on passing from the substituted phosphines of general formula $(PR_3)_2CdX_2$ [3,16] to the corresponding phosphonium salts in spite of a coordination change.

The Cd—Cl bond lengths in I are in good agreement with those of terminal bonds in the other tetrahedrally coordinated cadmium(II) structures, namely 2.428—2.486(6) Å (II), 2.432—2.465(1) Å (III) and 2.439—2.453(4) Å (IV). As expected, these figures are a little shorter than the terminal Cd—Cl distances reported for hexaammine cobalt(III) pentachlorocadmate (2.526(1), 2.561(2) Å) [17], in which the cadmate ion shows a trigonal bipyramidal coordination, and in the octahedral $Cd(HGlyGly)_2Cl_2$ (2.558(5), 2.568(5) Å) and $Cd(GlyGly)(OH_2)$ Cl (2.564(5) Å) structures [18]. Still longer (bridged) Cd—Cl

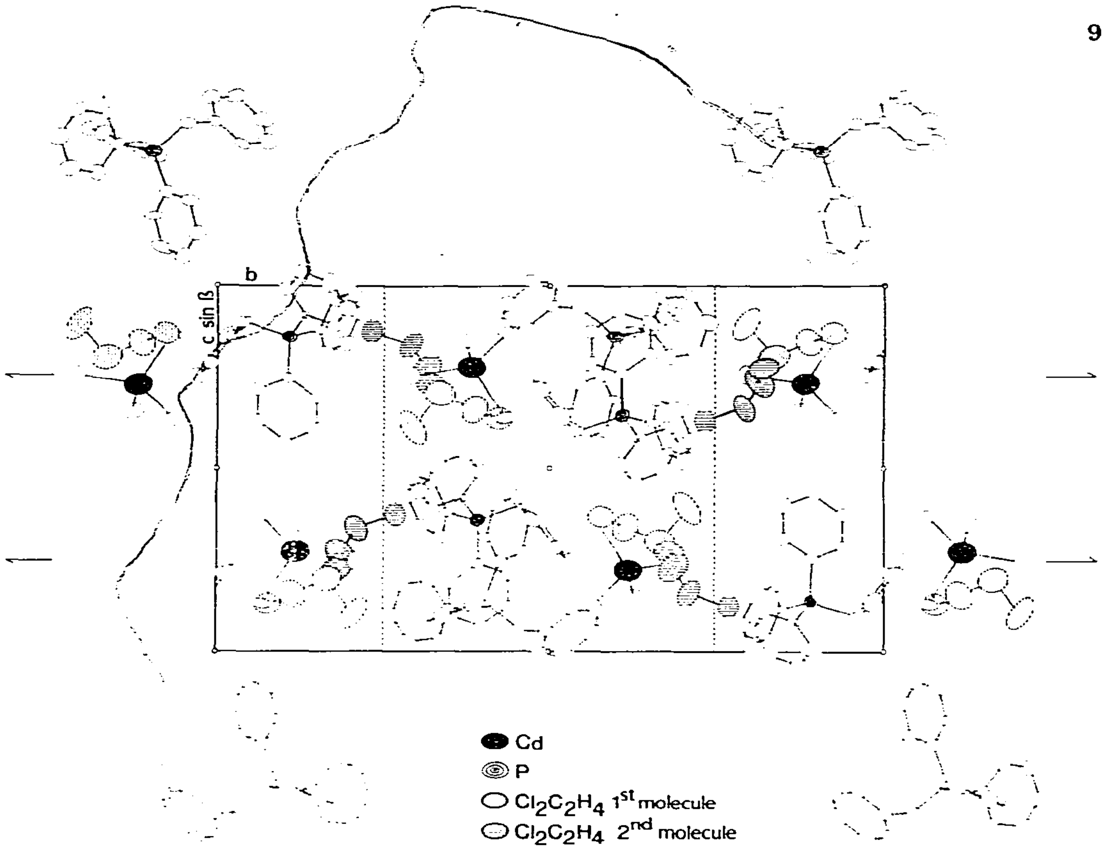

Fig. 2. Packing arrangement of the $[CdCl_4]^{2-} \cdot 2[(C_6H_5)_3PCH_2C_6H_5]^+ \cdot 2\ Cl_2C_2H_4$ clathrate as viewed down the *a* axis.

distances are observed in the octahedrally coordinated $CdCl_2$ structure [19]. The terminal Cd—Cl distances in chlorocadmate ions range from about 2.40 to 2.75 Å and this appears to be partly due to hydrogen bonding. The Cd—Cl distances reported for tris(ethylenediamine)cobalt(III) hexachlorocadmate(II) dichloride dihydrate [20], in which the cadmate ion shows a considerably distorted octahedral symmetry, vary from 2.588(3) and 2.617(2) to 2.765(2) Å, due to hydrogen bonding involving the chlorine atoms of the anion and the hydrogen atoms of the ethylene diamine rings. An analogous situation is reported for $CdCl_2 \cdot H_2O$ [21] with a distorted octahedral coordination around the cadmium atom and Cd—Cl distances ranging from 2.569(5) to 2.697(5) Å.

The two $[(C_6H_5)_3PCH_2C_6H_5]^+$ ions of I show a quasi-perfect tetrahedral symmetry with an average P—C(Phen) bond length of 1.79(2) Å (range 1.75—1.83 Å) and a P—CH_2 average distance of again 1.79(2) Å (range 1.78—1.80 Å); the mean value of the C—P—C bond angles is 109.5(4)° (range 106.6—112.6°C). These values are in good agreement with the literature values for organo-phosphonium ions [22]. The average value of the C—C bond lengths of the phenyl rings is 1.38(2) Å (range 1.29(4)—1.48(2)), while the average value of the endocyclic bond angles is 120.0(10)° (range 116(1)—124(2)°). The conformation of the phenyl rings and of the benzyl groups around the phosphorous atoms is clearly understood when the torsion angles around the

TABLE 4

MOLECULAR PARAMETERS. STANDARD DEVIATIONS IN PARENTHESES

a) Bond lengths (Å)

Cd—Cl(1)	2.439(4)	C(22)—C(23)	1.43(3)
Cd—Cl(2)	2.433(5)	C(23)—C(24)	1.36(4)
Cd—Cl(3)	2.438(6)	C(24)—C(25)	1.40(3)
Cd—Cl(4)	2.455(6)	C(25)—C(20)	1.37(2)
Average	2.441(5)	Average (phenyl)	1.37(3)
P(1)—C(1)	1.80(2)	C(26)—C(27)	1.52(2)
P(1)—C(7)	1.80(2)	C(27)—C(28)	1.38(2)
P(1)—C(13)	1.83(2)	C(28)—C(29)	1.37(3)
P(1)—C(19)	1.80(1)	C(29)—C(30)	1.40(3)
		C(30)—C(31)	1.32(3)
		C(31)—C(32)	1.42(3)
		C(32)—C(27)	1.37(2)
P(2)—C(26)	1.78(2)	Average(phenyl)	1.38(3)
P(2)—C(33)	1.75(2)		
P(2)—C(39)	1.78(2)		
P(2)—C(45)	1.76(2)	C(33)—C(34)	1.35(3)
		C(34)—C(35)	1.38(3)
		C(35)—C(36)	1.41(3)
		C(36)—C(37)	1.29(4)
C(1)—C(2)	1.39(2)	C(37)—C(38)	1.39(3)
C(2)—C(3)	1.39(3)	C(38)—C(33)	1.48(2)
C(3)—C(4)	1.37(2)	Average	1.38(2)
C(4)—C(5)	1.42(3)		
C(5)—C(6)	1.39(3)		
C(6)—C(1)	1.33(2)	C(39)—C(40)	1.32(2)
Average	1.38(2)	C(40)—C(41)	1.37(2)
		C(41)—C(42)	1.39(3)
C(7)—C(8)	1.39(3)	C(42)—C(43)	1.34(3)
C(8)—C(9)	1.42(3)	C(43)—C(44)	1.46(2)
C(9)—C(10)	1.39(2)	C(44)—C(39)	1.36(3)
C(10)—C(11)	1.36(3)	Average	1.37(3)
C(11)—C(12)	1.38(3)		
C(12)—C(7)	1.35(2)	C(45)—C(46)	1.37(3)
Average	1.38(2)	C(46)—C(47)	1.41(3)
		C(47)—C(48)	1.34(3)
C(13)—C(14)	1.34(3)	C(48)—C(49)	1.40(3)
C(14)—C(15)	1.41(3)	C(49)—C(50)	1.32(3)
C(15)—C(16)	1.37(4)	C(50)—C(45)	1.47(3)
C(16)—C(17)	1.30(4)	Average	1.39(3)
C(17)—C(18)	1.40(3)		
C(18)—C(13)	1.35(3)		
Average	1.36(4)	Cl(5)—C(51)	1.70(3)
		Cl(6)—C(52)	1.74(3)
		C(51)—C(52)	1.22(5)
C(19)—C(20)	1.50(3)	Cl(7)—C(53)	1.73(4)
C(20)—C(21)	1.35(3)	Cl(8)—C(54)	1.77(4)
C(21)—C(22)	1.30(3)	C(53)—C(54)	1.47(5)

b) Bond angles (degrees)

Cl(1)—Cd—Cl(2)	110.0(1)	Cl(2)—Cd—Cl(4)	111.4(1)
Cl(1)—Cd—Cl(3)	108.6(1)	Cl(3)—Cd—Cl(4)	112.5(1)
Cl(1)—Cd—Cl(4)	105.8(1)	Average	109.5(1)
Cl(2)—Cd—Cl(3)	108.5(1)		

TABLE 4 (continued)

C(1)—P(1)—C(7)	106.7(5)
C(1)—P(1)—C(13)	111.1(4)
C(1)—P(1)—C(19)	112.6(4)
C(7)—P(1)—C(13)	108.2(4)
C(7)—P(1)—C(19)	111.5(4)
C(13)—P(1)—C(19)	106.8(4)
Average	109.5(4)

C(26)—P(2)—C(33)	112.2(5)
C(26)—P(2)—C(39)	112.5(5)
C(26)—P(2)—C(45)	107.9(5)
C(33)—P(2)—C(39)	106.6(4)
C(33)—P(2)—C(45)	109.8(4)
C(39)—P(2)—C(45)	107.7(4)
Average	109.5(4)

P(1)—C(1)—C(2)	116.3(8)
P(1)—C(1)—C(6)	121.8(9)
P(1)—C(7)—C(8)	118.5(10)
P(1)—C(7)—C(12)	122.4(10)
P(1)—C(13)—C(14)	118.4(10)
P(1)—C(13)—C(18)	115.2(9)
P(1)—C(19)—C(20)	114.0(6)
C(19)—C(20)—C(21)	124.9(10)
C(19)—C(20)—C(25)	119.3(9)

P(2)—C(26)—C(27)	111.8(7)
C(26)—C(27)—C(28)	118.5(8)
C(26)—C(27)—C(32)	119.9(8)
P(2)—C(33)—C(34)	122.0(10)
P(2)—C(33)—C(38)	117.6(7)
P(2)—C(39)—C(40)	121.1(8)
P(2)—C(39)—C(44)	117.7(8)
P(2)—C(45)—C(46)	123.4(10)
P(2)—C(45)—C(50)	116.6(8)

Cl(5)—C(51)—C(52)	126.9(7)
C(51)—C(52)—Cl(6)	123.7(8)
Cl(7)—C(53)—C(54)	110.4(7)
C(53)—C(54)—Cl(8)	103.8(10)

c) Torsion angles (degrees)

C(20)—C(19)—P(1)—C(1)	65
C(20)—C(19)—P(1)—C(7)	185
C(20)—C(19)—P(1)—C(13)	—57
C(27)—C(26)—P(2)—C(33)	—74
C(27)—C(26)—P(2)—C(39)	46
C(27)—C(26)—P(2)—C(45)	165
P(1)—C(19)—C(20)—C(21)	—91
P(1)—C(19)—C(20)—C(25)	88
P(2)—C(26)—C(27)—C(28)	—95
P(2)—C(26)—C(27)—C(32)	83
Cl(5)—C(51)—C(52)—Cl(6)	41
Cl(7)—C(53)—C(54)—Cl(8)	—79
C(19)—P(1)—C(1)—C(2)	39
C(19)—P(1)—C(1)—C(6)	210
C(19)—P(1)—C(7)—C(8)	8
C(19)—P(1)—C(7)—C(12)	189
C(19)—P(1)—C(13)—C(14)	93
C(19)—P(1)—C(13)—C(18)	—81
C(26)—P(2)—C(33)—C(34)	146
C(26)—P(2)—C(33)—C(38)	—44
C(26)—P(2)—C(39)—C(40)	106
C(26)—P(2)—C(39)—C(44)	—70
C(26)—P(2)—C(45)—C(46)	—40
C(26)—P(2)—C(45)—C(50)	145

d) Non-bonded interactions (Å)

Cd—H(2)	3.74
Cd—H(531)	3.44
Cd—H(542)	3.75
Cd—H(21)	3.82
Cl(1)—H(3)	2.73
Cl(1)—C(3)	3.70
Cl(1)—H(531)	3.07
Cl(2)—H(542)	2.50
Cl(2)—C(54)	3.50

Cl(3)—H(21)	3.18
Cl(3)—H(22)	3.31
Cl(3)—H(511)	3.25
Cl(3)—H(512)	2.78
Cl(3)—H(521)	2.90
Cl(3)—C(51)	3.40
Cl(3)—C(52)	3.56
Cl(4)—H(2)	2.93
Cl(4)—H(192)	2.60
C(6)—C(14)	3.19
C(27)—C(44)	3.21
C(28)—C(39)	3.47
C(28)—C(44)	3.27
C(34)—C(44)	3.21
C(34)—C(50)	3.55
C(40)—C(46)	3.46
Cl(5)—Cl(6)	3.37
Cl(7)—Cl(8)	3.29

P—CH_2 bonds are considered. The P—C(Phen) bonds are nearly staggered (*gauche*+, *gauche*— and *trans*) in respect of the CH_2—C(Phen) bond of the benzyl residues. In Table 4 are also reported the torsion angles around the P—C(Phen) bonds with respect to the P—CH_2 bonds. These values are intermediate between the staggered and eclipsed conformations.

The bond lengths and angles found in I for the $ClCH_2CH_2Cl$ solvent molecules are unreliable. This derives from the fact that these molecules are affected by high positional disorder. As mentioned in the preceeding sections, the crystals of I lose solvent very easily even at room temperature and atmospheric pressure. Our attempts to stabilize the structure by sealing off the Lindemann glass capillary tubes filled with dry nitrogen only partially relieved the problem as shown by the intensity diminution of the monitoring reflections during the intensity data collection. However, it is clear that the two chlorine atoms of both molecules are nearly in *gauche* conformations.

The arrangement of the ions and of the solvent molecules in the unit cell is shown in Fig. 2. The most remarkable aspect of the packing is that two solvent molecules are disposed around each $[CdCl_4]^{2-}$ ion while the phosphonium ions are far apart, with very few interactions with the $[CdCl_4]^{2-}$ ions. The Van der Waals distances associated with the strongest Cd ... H, Cl ... H, Cl ... C and C ... C interactions are 3.16, 2.50, 3.40 and 3.60 Å, respectively.

Acknowledgements

Thanks are due to Dr. G. Moggi (DIMP, Linate) for preparation of the compound.

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