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Crystal structure of dichloro-[1-diphenylphosphinyloxy-2,2-bis(diphenylphosphinyloxymethyl)propane]ruthenium(II) solvate, $C_{82}H_{78}Cl_4O_6P_6Ru_2 \cdot 8CHCl_3 \cdot CH_3OH \cdot 5H_2O$, *a novel tridentate phosphinite-Ru complex used as a model of heterogenized oxidation catalyst*

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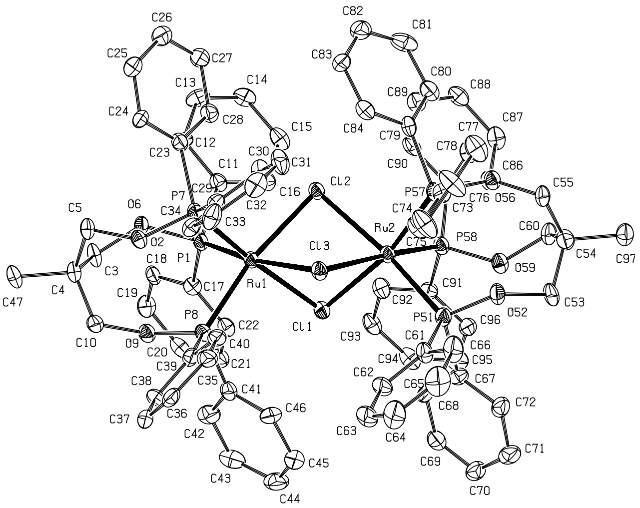

Abstract

$C_{91}H_{100}Cl_{28}O_{12}P_6Ru_2$, monoclinic, $P12_1/a1$ (No. 14), $a = 21.984(7)$ Å, $b = 25.643(8)$ Å, $c = 23.102(7)$ Å, $\beta = 114.54(3)°$, $V = 111847$ Å^3, $Z = 4$, $R_{gt}(F) = 0.104$, $wR_{ref}(F^2) = 0.322$, $T = 110$ K.

Source of material

The soluble reference catalyst was obtained from dichlorotetrakis(dimethylsulphoxide)ruthenium(II) and 1,1,1-tris(diphenylphosphinoxymethyl)-ethane in refluxing CH_2Cl_2. Ligand exchange furnished dichloro-[1-diphenylphosphinyloxy-2,2-bis(diphenylphosphinyloxymethyl)propane]ruthenium(II), purified by chromatography on Sephadex gel (elution with methanol; yield: 64%) and characterized by IR, ^{31}P-NMR and mass spectroscopy [1]. Recrystallization from moist $CHCl_3$ gave the sample (orange solid; mp 456.2 K – 457.6 K) presently analyzed by X-ray diffraction.

Experimental details

All the H atoms were calculated except those of the five water molecules and that of the OH of ethanol which were not located. The H atoms were refined with a common isotropic temperature factor ($U_{iso} = 0.074(5)$ Å^2). Restraints were applied on C—Cl of the 8 chloroform molecules and on C—O bond lengths of the methanol. The final R values are relatively high probably because it was not possible to include in the refinement the residual electron density corresponding to very disordered solvent molecules. The squeeze option of the PLATON program was applied to take into account this density in an optimal way [2,3].

Discussion

Nowadays, due to economical and environmental inciting, increasing attention is dedicated to recoverable catalysts and reagents [4]. In the field of transition metal catalysis, an attractive strategy consists in the of homogeneous catalysts, i.e. the attachment of homogeneous catalysts onto insoluble supports (polymer, silica, etc) via appropriate spacer-arms [5]. In this context, we recently developed a novel tridentate phosphinite-Ru (II) complex covalently bound on silica [6]. This material catalyzed the oxidation of alcohols into aldehydes, in the same way as the corresponding homogeneous catalyst, and could be recycled [1]. Although the novel tridentate complex appeared to exist mainly as the monomeric form in solution from NMR analysis [1], at the solid state it showed a dimeric structure very similar to that of the related monodentate complex [7]. The Ru—Ru distance of 3.496(2) Å is just above the upper limit of the range (3.26 Å – 3.46 Å) of reported values for other $Ru_2(\mu_2Cl)_3$ complexes [8]. The mean values for Ru—Cl and Ru—P bond lengths are 2.504(3) Å and 2.278(4) Å, respectively. These values are very similar to those observed for the dimeric Ru(II) methoxydiphenylphosphane complex [7].

In the structure, we have localized eight chloroform, five water and one methanol molecules. The methanol and all five water molecules are hydrogen-bonded with distances ranging from 2.47 Å to 2.98 Å. There is no specific contact between the complex and the solvent molecules.

Table 1. Data collection and handling.

Crystal:	orange parallelepiped, size 0.20 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	10.20 cm^{-1}
Diffractometer, scan mode:	MAR345, 100 images, $\Delta\varphi = 2°$
$2\theta_{max}$:	41.62°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	35734, 12009
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8541
$N(param)_{refined}$:	1254
Programs:	SHELXS-97 [9], SHELXL-97 [10], PLATON [3]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	4e	0.2214	0.5433	0.1413	0.074(5)
H(3B)	4e	0.1789	0.5872	0.0944	0.074
H(5A)	4e	0.2310	0.6766	0.1542	0.074
H(5B)	4e	0.2090	0.6884	0.2094	0.074
H(10A)	4e	0.2542	0.6025	0.2867	0.074
H(10B)	4e	0.2100	0.5542	0.2531	0.074
H(12)	4e	0.2737	0.6309	0.0271	0.074
H(13)	4e	0.2844	0.6413	–0.0685	0.074
H(14)	4e	0.3724	0.6070	–0.0808	0.074
H(15)	4e	0.4494	0.5542	–0.0031	0.074
H(16)	4e	0.4404	0.5412	0.0927	0.074
H(18)	4e	0.2356	0.5154	0.0509	0.074
H(19)	4e	0.2025	0.4299	0.0242	0.074
H(20)	4e	0.2719	0.3627	0.0821	0.074
H(21)	4e	0.3720	0.3815	0.1678	0.074
H(22)	4e	0.4044	0.4668	0.1943	0.074
H(24)	4e	0.2895	0.7642	0.1845	0.074
H(25)	4e	0.2655	0.8223	0.1030	0.074
H(26)	4e	0.3070	0.8139	0.0270	0.074
H(27)	4e	0.3764	0.7464	0.0325	0.074
H(28)	4e	0.4005	0.6821	0.1134	0.074
H(30)	4e	0.4852	0.7350	0.2461	0.074
H(31)	4e	0.5496	0.7962	0.3181	0.074
H(32)	4e	0.5215	0.8233	0.4013	0.074
H(33)	4e	0.4288	0.7872	0.4094	0.074
H(34)	4e	0.3650	0.7225	0.3410	0.074
H(36)	4e	0.3137	0.5450	0.3757	0.074
H(37)	4e	0.3183	0.5762	0.4716	0.074
H(38)	4e	0.3893	0.6463	0.5193	0.074
H(39)	4e	0.4606	0.6783	0.4783	0.074
H(40)	4e	0.4553	0.6445	0.3815	0.074
H(42)	4e	0.3272	0.4561	0.2603	0.074
H(43)	4e	0.3696	0.3739	0.2991	0.074
H(44)	4e	0.4746	0.3677	0.3883	0.074
H(45)	4e	0.5324	0.4411	0.4354	0.074
H(46)	4e	0.4897	0.5221	0.3970	0.074
H(47A)	4e	0.1123	0.6326	0.1378	0.074
H(47B)	4e	0.1291	0.6301	0.2107	0.074
H(47C)	4e	0.1164	0.5785	0.1710	0.074
H(53A)	4e	0.8093	0.5146	0.3704	0.074
H(53B)	4e	0.8540	0.5590	0.4146	0.074
H(55A)	4e	0.8095	0.6491	0.3474	0.074
H(55B)	4e	0.8319	0.6513	0.2911	0.074
H(60A)	4e	0.7767	0.5654	0.2214	0.074
H(60B)	4e	0.8154	0.5152	0.2569	0.074

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(62)	4e	0.5931	0.5258	0.4183	0.074
H(63)	4e	0.5825	0.5441	0.5132	0.074
H(64)	4e	0.6623	0.5887	0.5910	0.074
H(65)	4e	0.7513	0.6261	0.5762	0.074
H(66)	4e	0.7611	0.6126	0.4786	0.074
H(68)	4e	0.6006	0.4570	0.3169	0.074
H(69)	4e	0.6142	0.3719	0.3465	0.074
H(70)	4e	0.7051	0.3399	0.4239	0.074
H(71)	4e	0.7947	0.3966	0.4780	0.074
H(72)	4e	0.7848	0.4859	0.4518	0.074
H(74)	4e	0.6514	0.6721	0.3918	0.074
H(75)	4e	0.6921	0.7331	0.4700	0.074
H(76)	4e	0.7550	0.8034	0.4630	0.074
H(77)	4e	0.7909	0.8039	0.3829	0.074
H(78)	4e	0.7486	0.7413	0.3005	0.074
H(80)	4e	0.6791	0.6736	0.1539	0.074
H(81)	4e	0.6178	0.7274	0.0668	0.074
H(82)	4e	0.5412	0.7849	0.0724	0.074
H(83)	4e	0.5185	0.7878	0.1574	0.074
H(84)	4e	0.5786	0.7391	0.2467	0.074
H(86)	4e	0.7133	0.5010	0.1414	0.074
H(87)	4e	0.7101	0.5172	0.0436	0.074
H(88)	4e	0.6330	0.5816	–0.0220	0.074
H(89)	4e	0.5587	0.6189	0.0122	0.074
H(90)	4e	0.5678	0.6034	0.1144	0.074
H(92)	4e	0.5220	0.4845	0.1437	0.074
H(93)	4e	0.4845	0.3982	0.1274	0.074
H(94)	4e	0.5587	0.3306	0.1668	0.074
H(95)	4e	0.6694	0.3468	0.2290	0.074
H(96)	4e	0.7082	0.4319	0.2532	0.074
H(97A)	4e	0.9132	0.5372	0.3409	0.074
H(97B)	4e	0.9235	0.5934	0.3702	0.074
H(97C)	4e	0.9058	0.5860	0.2976	0.074
H(100)	4e	0.9537	0.5315	0.1585	0.074
H(200)	4e	0.9695	0.3918	0.0874	0.074
H(300)	4e	0.1009	0.5402	0.3171	0.074
H(400)	4e	0.4204	0.2184	0.1269	0.074
H(500)	4e	0.9200	0.3818	0.2022	0.074
H(600)	4e	0.0686	0.2934	0.1269	0.074
H(700)	4e	0.1069	0.3912	0.1971	0.074
H(800)	4e	0.5483	0.2141	0.2835	0.074
H(90A)	4e	0.4582	0.2870	0.4103	0.074
H(90B)	4e	0.3948	0.2569	0.3632	0.074
H(90C)	4e	0.4467	0.2287	0.4238	0.074

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	4e	0.43094(5)	0.59733(4)	0.23600(5)	0.0376(7)	0.0528(7)	0.0406(7)	0.0011(5)	0.0200(5)	0.0019(5)
Cl(1)	4e	0.5085(2)	0.5217(1)	0.2566(1)	0.045(2)	0.057(2)	0.052(2)	0.002(2)	0.026(2)	0.002(2)
Cl(2)	4e	0.5038(1)	0.6245(1)	0.1828(1)	0.041(2)	0.058(2)	0.042(2)	–0.001(2)	0.021(2)	0.000(2)
Cl(3)	4e	0.5365(2)	0.6280(1)	0.3268(1)	0.044(2)	0.065(2)	0.043(2)	0.001(2)	0.023(2)	–0.004(2)
Ru(2)	4e	0.60122(5)	0.58414(4)	0.27240(5)	0.0384(7)	0.0581(7)	0.0382(7)	0.0004(5)	0.0193(5)	–0.0008(5)
P(1)	4e	0.3469(2)	0.5691(1)	0.1444(2)	0.037(2)	0.057(2)	0.045(2)	0.000(2)	0.021(2)	0.000(2)
O(2)	4e	0.2767(4)	0.5993(3)	0.1282(4)	0.033(5)	0.058(5)	0.046(5)	0.005(4)	0.018(4)	–0.002(4)
C(3)	4e	0.2179(6)	0.5806(6)	0.1337(7)	0.034(8)	0.08(1)	0.064(9)	–0.011(7)	0.028(7)	–0.024(8)
C(4)	4e	0.2097(6)	0.6097(5)	0.1916(6)	0.033(7)	0.061(9)	0.059(9)	–0.002(7)	0.022(7)	–0.009(7)
C(5)	4e	0.2356(6)	0.6654(5)	0.1959(6)	0.037(8)	0.063(9)	0.061(9)	0.005(6)	0.024(7)	–0.010(7)
O(6)	4e	0.3076(4)	0.6688(3)	0.2422(4)	0.047(5)	0.061(6)	0.058(6)	0.004(4)	0.033(5)	0.003(5)
P(7)	4e	0.3729(2)	0.6731(1)	0.2263(2)	0.037(2)	0.059(2)	0.044(2)	0.002(2)	0.019(2)	0.002(2)
P(8)	4e	0.3790(2)	0.5627(1)	0.2943(2)	0.049(2)	0.056(2)	0.051(2)	0.002(2)	0.029(2)	0.003(2)
O(9)	4e	0.3012(4)	0.5516(3)	0.2547(4)	0.049(5)	0.059(6)	0.052(5)	0.001(4)	0.027(5)	–0.001(4)
C(10)	4e	0.2420(6)	0.5792(5)	0.2506(6)	0.051(8)	0.056(9)	0.057(9)	0.005(7)	0.032(7)	0.005(7)
C(11)	4e	0.3559(6)	0.5840(5)	0.0700(6)	0.046(8)	0.060(9)	0.043(8)	–0.007(7)	0.021(7)	–0.006(7)
C(12)	4e	0.3089(7)	0.6152(5)	0.0213(6)	0.057(9)	0.064(9)	0.045(9)	0.003(7)	0.020(8)	0.017(7)
C(13)	4e	0.3159(8)	0.6220(6)	–0.0357(6)	0.09(1)	0.06(1)	0.035(8)	0.008(9)	0.012(8)	0.004(7)
C(14)	4e	0.3675(8)	0.6008(6)	–0.0433(6)	0.08(1)	0.07(1)	0.028(8)	–0.008(9)	0.030(8)	–0.009(7)
C(15)	4e	0.4146(7)	0.5695(6)	0.0038(7)	0.061(9)	0.07(1)	0.06(1)	–0.026(8)	0.034(9)	–0.026(8)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(16)	4*e*	0.4090(6)	0.5614(5)	0.0609(6)	0.049(8)	0.067(9)	0.041(8)	0.000(7)	0.021(7)	–0.004(7)
C(17)	4*e*	0.3225(6)	0.4998(5)	0.1269(6)	0.050(8)	0.051(8)	0.043(8)	–0.004(7)	0.019(7)	–0.005(7)
C(18)	4*e*	0.2626(6)	0.4883(6)	0.0747(6)	0.037(8)	0.07(1)	0.054(9)	–0.004(7)	0.026(7)	0.001(8)
C(19)	4*e*	0.2430(7)	0.4373(6)	0.0582(7)	0.052(9)	0.07(1)	0.060(9)	–0.006(9)	0.020(8)	–0.015(9)
C(20)	4*e*	0.2844(8)	0.3972(6)	0.0930(7)	0.07(1)	0.06(1)	0.08(1)	–0.021(9)	0.05(1)	–0.014(9)
C(21)	4*e*	0.3445(7)	0.4085(5)	0.1443(7)	0.06(1)	0.06(1)	0.07(1)	0.001(7)	0.037(9)	0.000(7)
C(22)	4*e*	0.3636(6)	0.4595(5)	0.1606(6)	0.045(8)	0.06(1)	0.052(8)	–0.010(7)	0.022(7)	–0.007(7)
C(23)	4*e*	0.3474(6)	0.7168(6)	0.1561(6)	0.043(8)	0.08(1)	0.049(8)	–0.002(7)	0.022(7)	0.007(7)
C(24)	4*e*	0.3065(6)	0.7597(5)	0.1541(6)	0.044(8)	0.07(1)	0.054(9)	0.018(7)	0.018(7)	0.018(8)
C(25)	4*e*	0.2931(7)	0.7940(6)	0.1056(8)	0.06(1)	0.07(1)	0.10(1)	0.023(8)	0.04(1)	0.03(1)
C(26)	4*e*	0.3181(8)	0.7894(7)	0.0595(8)	0.08(1)	0.10(1)	0.08(1)	0.03(1)	0.04(1)	0.03(1)
C(27)	4*e*	0.3583(8)	0.7492(7)	0.0623(7)	0.07(1)	0.10(1)	0.06(1)	0.02(1)	0.040(9)	0.023(9)
C(28)	4*e*	0.3736(6)	0.7106(6)	0.1116(6)	0.049(8)	0.07(1)	0.044(8)	–0.005(7)	0.019(7)	0.000(7)
C(29)	4*e*	0.4178(6)	0.7220(5)	0.2843(6)	0.051(8)	0.044(8)	0.048(8)	0.005(6)	0.018(7)	–0.002(6)
C(30)	4*e*	0.4741(7)	0.7450(5)	0.2792(7)	0.053(9)	0.063(9)	0.063(9)	–0.003(8)	0.025(8)	–0.013(8)
C(31)	4*e*	0.5127(7)	0.7820(6)	0.3221(8)	0.053(9)	0.07(1)	0.12(1)	–0.019(8)	0.04(1)	–0.02(1)
C(32)	4*e*	0.4960(8)	0.7983(6)	0.3722(7)	0.07(1)	0.07(1)	0.06(1)	–0.003(9)	0.011(9)	–0.027(8)
C(33)	4*e*	0.4402(8)	0.7759(7)	0.3770(7)	0.06(1)	0.10(1)	0.052(9)	0.02(1)	0.005(8)	–0.017(9)
C(34)	4*e*	0.4008(7)	0.7375(5)	0.3356(6)	0.053(8)	0.058(9)	0.043(8)	0.011(7)	0.013(7)	0.001(7)
C(35)	4*e*	0.3831(6)	0.5918(5)	0.3687(6)	0.043(8)	0.063(9)	0.044(8)	0.015(7)	0.018(7)	0.005(7)
C(36)	4*e*	0.3431(7)	0.5719(6)	0.3962(6)	0.059(9)	0.08(1)	0.047(9)	0.008(7)	0.038(8)	0.012(7)
C(37)	4*e*	0.3450(7)	0.5906(6)	0.4533(8)	0.043(9)	0.09(1)	0.07(1)	0.017(8)	0.025(8)	0.027(9)
C(38)	4*e*	0.3887(7)	0.6319(7)	0.4821(7)	0.06(1)	0.10(1)	0.047(9)	0.04(1)	0.027(8)	0.029(9)
C(39)	4*e*	0.4307(8)	0.6518(6)	0.4574(7)	0.08(1)	0.07(1)	0.08(1)	0.023(8)	0.05(1)	0.024(9)
C(40)	4*e*	0.4274(7)	0.6313(6)	0.3992(6)	0.061(9)	0.07(1)	0.045(8)	0.014(8)	0.031(8)	0.012(7)
C(41)	4*e*	0.4053(7)	0.4989(6)	0.3231(7)	0.053(9)	0.06(1)	0.07(1)	0.007(8)	0.039(9)	0.004(8)
C(42)	4*e*	0.3685(9)	0.4531(6)	0.2948(7)	0.10(1)	0.08(1)	0.06(1)	0.02(1)	0.06(1)	0.012(9)
C(43)	4*e*	0.394(1)	0.4038(6)	0.3181(9)	0.12(2)	0.06(1)	0.08(1)	–0.01(1)	0.06(1)	0.003(9)
C(44)	4*e*	0.457(1)	0.4002(7)	0.372(1)	0.12(2)	0.06(1)	0.12(2)	0.03(1)	0.08(2)	0.04(1)
C(45)	4*e*	0.4916(8)	0.4438(7)	0.4003(8)	0.07(1)	0.08(1)	0.08(1)	0.01(1)	0.04(1)	0.02(1)
C(46)	4*e*	0.4659(8)	0.4926(6)	0.3766(7)	0.08(1)	0.06(1)	0.07(1)	0.012(8)	0.03(1)	0.026(9)
C(47)	4*e*	0.1349(6)	0.6131(6)	0.1763(7)	0.039(8)	0.09(1)	0.07(1)	–0.013(7)	0.031(7)	–0.013(8)
P(51)	4*e*	0.6816(2)	0.5520(2)	0.3640(2)	0.044(2)	0.069(2)	0.043(2)	0.007(2)	0.022(2)	0.002(2)
O(52)	4*e*	0.7543(4)	0.5754(4)	0.3802(4)	0.036(5)	0.083(7)	0.055(6)	0.000(5)	0.018(5)	–0.002(5)
C(53)	4*e*	0.8147(6)	0.5521(6)	0.3757(7)	0.048(8)	0.08(1)	0.064(9)	0.001(7)	0.040(8)	–0.014(8)
C(54)	4*e*	0.8242(7)	0.5758(6)	0.3184(7)	0.050(9)	0.08(1)	0.07(1)	–0.003(8)	0.024(8)	0.004(9)
C(55)	4*e*	0.8036(6)	0.6330(5)	0.3074(6)	0.032(7)	0.07(1)	0.053(8)	–0.005(6)	0.011(7)	–0.009(7)
O(56)	4*e*	0.7345(4)	0.6375(3)	0.2625(4)	0.043(5)	0.069(6)	0.044(5)	–0.001(4)	0.019(5)	–0.003(4)
P(57)	4*e*	0.6686(2)	0.6517(1)	0.2744(2)	0.038(2)	0.063(2)	0.042(2)	–0.002(2)	0.019(2)	–0.005(2)
P(58)	4*e*	0.6475(2)	0.5351(1)	0.2183(2)	0.039(2)	0.060(2)	0.040(2)	–0.001(2)	0.018(2)	–0.002(2)
O(59)	4*e*	0.7247(4)	0.5226(3)	0.2591(4)	0.041(5)	0.071(6)	0.041(5)	–0.008(4)	0.015(4)	–0.011(4)
C(60)	4*e*	0.7872(6)	0.5437(6)	0.2587(6)	0.037(8)	0.07(1)	0.052(9)	0.000(7)	0.012(7)	–0.012(8)
C(61)	4*e*	0.6769(7)	0.5691(6)	0.4394(6)	0.047(8)	0.09(1)	0.040(8)	0.000(8)	0.024(8)	–0.006(8)
C(62)	4*e*	0.6242(7)	0.5469(6)	0.4492(7)	0.07(1)	0.10(1)	0.049(9)	0.002(9)	0.036(8)	0.013(8)
C(63)	4*e*	0.6189(9)	0.5568(7)	0.5070(8)	0.08(1)	0.13(2)	0.06(1)	0.01(1)	0.05(1)	0.01(1)
C(64)	4*e*	0.666(1)	0.584(1)	0.5524(9)	0.09(2)	0.20(2)	0.05(1)	0.04(2)	0.04(1)	0.01(1)
C(65)	4*e*	0.720(1)	0.6064(8)	0.5439(8)	0.10(1)	0.16(2)	0.05(1)	–0.01(1)	0.02(1)	–0.03(1)
C(66)	4*e*	0.7257(9)	0.5985(8)	0.4854(7)	0.07(1)	0.16(2)	0.05(1)	0.02(1)	0.030(9)	–0.01(1)
C(67)	4*e*	0.6925(7)	0.4809(5)	0.3809(6)	0.059(9)	0.053(8)	0.039(8)	0.005(8)	0.019(7)	0.002(7)
C(68)	4*e*	0.6403(7)	0.4459(6)	0.3495(7)	0.053(9)	0.06(1)	0.062(9)	0.024(8)	0.027(8)	0.020(8)
C(69)	4*e*	0.6493(8)	0.3948(6)	0.3681(8)	0.07(1)	0.07(1)	0.09(1)	0.001(9)	0.05(1)	0.01(1)
C(70)	4*e*	0.7025(8)	0.3751(7)	0.4135(7)	0.07(1)	0.09(1)	0.05(1)	0.02(1)	0.024(9)	0.017(9)
C(71)	4*e*	0.756(1)	0.4092(7)	0.4459(8)	0.10(1)	0.10(2)	0.06(1)	0.04(1)	0.05(1)	0.03(1)
C(72)	4*e*	0.7500(7)	0.4630(7)	0.4297(7)	0.06(1)	0.09(1)	0.06(1)	0.022(9)	0.030(9)	0.013(9)
C(73)	4*e*	0.6986(6)	0.6980(5)	0.3407(6)	0.052(8)	0.047(8)	0.059(9)	–0.003(7)	0.026(7)	–0.008(7)
C(74)	4*e*	0.6801(7)	0.6979(6)	0.3894(6)	0.07(1)	0.08(1)	0.048(8)	–0.027(8)	0.040(8)	–0.027(8)
C(75)	4*e*	0.7032(9)	0.7354(8)	0.4353(9)	0.11(1)	0.13(2)	0.10(1)	–0.03(1)	0.09(1)	–0.04(1)
C(76)	4*e*	0.7425(9)	0.7770(7)	0.4326(8)	0.11(1)	0.10(1)	0.08(1)	–0.06(1)	0.07(1)	–0.05(1)
C(77)	4*e*	0.7620(8)	0.7780(7)	0.3844(8)	0.08(1)	0.09(1)	0.10(1)	–0.04(1)	0.04(1)	–0.04(1)
C(78)	4*e*	0.7381(7)	0.7392(6)	0.3355(7)	0.062(9)	0.07(1)	0.058(9)	–0.009(8)	0.020(8)	–0.016(8)
C(79)	4*e*	0.6320(6)	0.6967(5)	0.2084(6)	0.032(7)	0.063(9)	0.062(9)	–0.011(7)	0.017(7)	–0.007(7)
C(80)	4*e*	0.6462(7)	0.6957(6)	0.1554(7)	0.059(9)	0.08(1)	0.06(1)	–0.012(8)	0.032(8)	–0.003(9)
C(81)	4*e*	0.6101(9)	0.7288(7)	0.1034(7)	0.11(1)	0.08(1)	0.05(1)	–0.04(1)	0.03(1)	–0.007(9)
C(82)	4*e*	0.5640(8)	0.7629(6)	0.1066(8)	0.07(1)	0.06(1)	0.07(1)	–0.007(9)	0.019(9)	0.011(9)
C(83)	4*e*	0.5514(7)	0.7651(6)	0.1571(8)	0.048(9)	0.08(1)	0.08(1)	0.003(8)	0.015(9)	0.03(1)
C(84)	4*e*	0.5858(7)	0.7347(6)	0.2100(8)	0.057(9)	0.07(1)	0.08(1)	–0.013(8)	0.032(9)	0.002(9)
C(85)	4*e*	0.6423(6)	0.5527(5)	0.1393(5)	0.033(7)	0.071(9)	0.024(7)	–0.004(7)	0.012(6)	0.006(7)
C(86)	4*e*	0.6836(6)	0.5259(5)	0.1157(6)	0.046(8)	0.07(1)	0.038(8)	–0.004(7)	0.019(7)	–0.010(7)
C(87)	4*e*	0.6818(7)	0.5349(6)	0.0576(6)	0.050(8)	0.08(1)	0.046(9)	–0.008(8)	0.021(7)	–0.022(8)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(88)	4*e*	0.6343(7)	0.5730(6)	0.0176(7)	0.07(1)	0.08(1)	0.056(9)	–0.005(9)	0.046(9)	–0.006(8)
C(89)	4*e*	0.5915(7)	0.5963(5)	0.0388(7)	0.055(9)	0.06(1)	0.07(1)	–0.003(7)	0.026(8)	0.001(8)
C(90)	4*e*	0.5965(7)	0.5865(6)	0.1003(6)	0.054(9)	0.08(1)	0.036(8)	–0.016(8)	0.027(7)	–0.005(8)
C(91)	4*e*	0.6180(7)	0.4662(5)	0.1998(6)	0.051(9)	0.063(9)	0.041(8)	0.002(7)	0.024(7)	0.004(7)
C(92)	4*e*	0.5515(7)	0.4571(6)	0.1618(6)	0.06(1)	0.06(1)	0.059(9)	0.000(7)	0.033(8)	–0.012(7)
C(93)	4*e*	0.5295(7)	0.4053(6)	0.1512(7)	0.056(9)	0.08(1)	0.055(9)	–0.016(9)	0.032(8)	–0.015(8)
C(94)	4*e*	0.5738(8)	0.3648(6)	0.1756(7)	0.07(1)	0.06(1)	0.08(1)	–0.018(9)	0.05(1)	–0.023(8)
C(95)	4*e*	0.6399(8)	0.3746(6)	0.2129(7)	0.08(1)	0.06(1)	0.06(1)	–0.001(9)	0.039(9)	–0.010(8)
C(96)	4*e*	0.6636(7)	0.4252(6)	0.2268(7)	0.058(9)	0.07(1)	0.059(9)	0.018(8)	0.036(8)	0.015(8)
C(97)	4*e*	0.8986(6)	0.5728(6)	0.3332(7)	0.050(9)	0.09(1)	0.054(9)	0.008(8)	0.021(7)	–0.004(8)
Cl(4)	4*e*	0.0114(2)	0.3368(2)	0.1815(2)	0.075(3)	0.088(3)	0.081(3)	–0.006(2)	0.035(2)	–0.004(2)
C(100)	4*e*	0.9360(8)	0.5671(9)	0.1502(7)	0.11(2)	0.17(2)	0.08(1)	0.00(2)	0.04(1)	–0.00(1)
Cl(5)	4*e*	0.8492(2)	0.5644(2)	0.1314(2)	0.069(3)	0.142(4)	0.090(3)	–0.029(3)	0.043(3)	–0.011(3)
Cl(6)	4*e*	0.9478(3)	0.5911(3)	0.0851(2)	0.080(3)	0.273(8)	0.074(3)	–0.048(4)	0.041(3)	0.000(4)
Cl(7)	4*e*	0.9787(3)	0.6036(3)	0.2161(3)	0.109(4)	0.248(8)	0.078(3)	–0.082(5)	0.037(3)	–0.025(4)
C(200)	4*e*	0.931(1)	0.4013(6)	0.049(1)	0.16(2)	0.10(2)	0.11(2)	–0.00(1)	0.06(2)	0.01(1)
Cl(8)	4*e*	0.8730(3)	0.4351(2)	0.0686(2)	0.110(4)	0.149(5)	0.092(4)	0.040(4)	0.045(3)	0.008(3)
Cl(9)	4*e*	0.9560(3)	0.4403(3)	0.0001(3)	0.113(4)	0.178(6)	0.117(4)	–0.025(4)	0.056(4)	0.027(4)
Cl(10)	4*e*	0.8900(4)	0.3429(3)	0.0064(3)	0.170(6)	0.136(5)	0.113(4)	0.023(4)	0.040(4)	–0.003(4)
C(300)	4*e*	0.1256(9)	0.5523(7)	0.3609(9)	0.11(2)	0.14(2)	0.08(1)	0.04(2)	0.03(1)	0.00(1)
Cl(11)	4*e*	0.1898(3)	0.5093(2)	0.4021(3)	0.092(3)	0.137(5)	0.101(4)	0.009(3)	0.034(3)	–0.003(3)
Cl(12)	4*e*	0.1581(3)	0.6162(3)	0.3610(3)	0.109(4)	0.181(6)	0.111(4)	0.057(4)	0.064(4)	0.051(4)
Cl(13)	4*e*	0.0710(3)	0.5574(3)	0.3990(4)	0.084(4)	0.217(8)	0.244(9)	0.007(4)	0.091(5)	0.021(7)
C(400)	4*e*	0.395(1)	0.2500(8)	0.127(1)	0.24(3)	0.11(2)	0.29(4)	0.05(2)	0.20(3)	0.04(2)
Cl(14)	4*e*	0.3984(3)	0.2948(2)	0.0738(3)	0.196(6)	0.086(3)	0.147(5)	–0.034(4)	0.119(5)	–0.024(3)
Cl(15)	4*e*	0.3146(4)	0.2360(3)	0.1167(5)	0.133(5)	0.170(7)	0.27(1)	–0.025(5)	0.099(7)	0.041(7)
Cl(16)	4*e*	0.4299(7)	0.2842(4)	0.2058(5)	0.49(2)	0.182(9)	0.22(1)	0.19(1)	0.21(1)	0.089(8)
C(500)	4*e*	0.9034(8)	0.3942(6)	0.2331(8)	0.11(2)	0.09(1)	0.11(2)	0.01(1)	0.06(1)	0.01(1)
Cl(17)	4*e*	0.8170(3)	0.4034(3)	0.1933(3)	0.086(4)	0.158(5)	0.129(5)	0.023(3)	0.033(3)	–0.024(4)
Cl(18)	4*e*	0.9459(3)	0.4525(2)	0.2674(3)	0.115(4)	0.134(5)	0.147(5)	–0.005(4)	0.051(4)	–0.032(4)
Cl(19)	4*e*	0.9208(4)	0.3462(3)	0.2926(4)	0.199(8)	0.164(7)	0.161(6)	0.019(6)	0.087(6)	0.040(5)
C(600)	4*e*	0.093(1)	0.2828(7)	0.1012(9)	0.23(3)	0.11(2)	0.17(2)	0.07(2)	0.15(2)	0.03(2)
Cl(20)	4*e*	0.0948(4)	0.3335(2)	0.0513(3)	0.196(7)	0.086(4)	0.173(6)	–0.008(4)	0.116(6)	–0.009(4)
Cl(21)	4*e*	0.0529(5)	0.2276(3)	0.0520(4)	0.250(9)	0.132(6)	0.154(6)	–0.027(6)	0.123(7)	0.001(5)
Cl(22)	4*e*	0.1735(5)	0.2650(7)	0.1485(8)	0.118(7)	0.53(3)	0.40(2)	0.09(1)	0.051(9)	0.26(2)
C(700)	4*e*	0.130(1)	0.4249(9)	0.207(1)	0.35(5)	0.44(6)	0.66(9)	–0.35(5)	0.44(6)	–0.50(7)
Cl(23)	4*e*	0.0794(4)	0.4751(4)	0.2100(7)	0.131(6)	0.168(8)	0.39(2)	–0.011(6)	0.069(9)	–0.011(9)
Cl(24)	4*e*	0.1588(8)	0.4435(5)	0.1546(5)	0.51(2)	0.28(1)	0.23(1)	–0.25(1)	0.27(1)	–0.136(9)
Cl(25)	4*e*	0.1922(6)	0.4275(5)	0.2834(4)	0.26(1)	0.31(1)	0.134(7)	–0.13(1)	0.011(7)	–0.003(8)
C(800)	4*e*	0.584(1)	0.2193(8)	0.326(1)	0.12(2)	0.18(3)	0.13(2)	0.00(2)	0.04(2)	–0.04(2)
Cl(26)	4*e*	0.5527(5)	0.2560(4)	0.3690(5)	0.25(1)	0.184(8)	0.172(7)	–0.003(7)	0.045(7)	–0.073(7)
Cl(27)	4*e*	0.6483(6)	0.2492(5)	0.3169(8)	0.26(1)	0.27(1)	0.50(2)	–0.16(1)	0.22(2)	–0.21(2)
Cl(28)	4*e*	0.6098(7)	0.1555(6)	0.3618(7)	0.23(1)	0.32(2)	0.30(2)	0.10(1)	0.01(1)	0.01(1)
OW(1)	4*e*	1.0042(6)	0.3688(4)	0.4831(4)	0.14(1)	0.077(7)	0.018(5)	0.003(7)	0.026(6)	0.020(5)
OW(2)	4*e*	1.0824(7)	0.4294(6)	0.4428(5)	0.14(1)	0.14(1)	0.055(7)	–0.08(1)	–0.016(8)	0.014(8)
OW(3)	4*e*	1.1162(6)	0.3331(6)	0.5055(5)	0.110(9)	0.19(1)	0.051(7)	–0.08(1)	0.026(7)	0.006(8)
OW(4)	4*e*	0.8188(9)	0.3100(6)	0.386(1)	0.18(2)	0.12(1)	0.59(4)	–0.04(1)	0.29(2)	–0.17(2)
OW(5)	4*e*	0.320(1)	0.2651(6)	0.301(1)	0.20(2)	0.10(1)	0.22(2)	–0.02(1)	0.10(2)	0.03(1)
O(900)	4*e*	0.390(1)	0.2779(9)	0.442(1)	0.18(2)	0.21(2)	0.30(3)	–0.03(2)	0.20(2)	0.02(2)
C(900)	4*e*	0.425(1)	0.2613(8)	0.407(1)	0.21(3)	0.06(2)	0.29(4)	–0.11(2)	0.02(3)	0.02(2)

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