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Crystal structure of bis(bis(3-methoxysalicylaldehydato)copper(II)) hexakis(adamantylammonium) hexaperchlorate dihydrate, $[\{Cu(C_8H_7O_3)_2\}_2] \cdot (C_{10}H_{15}NH_3)_6(ClO_4)_6 \cdot 2H_2O$

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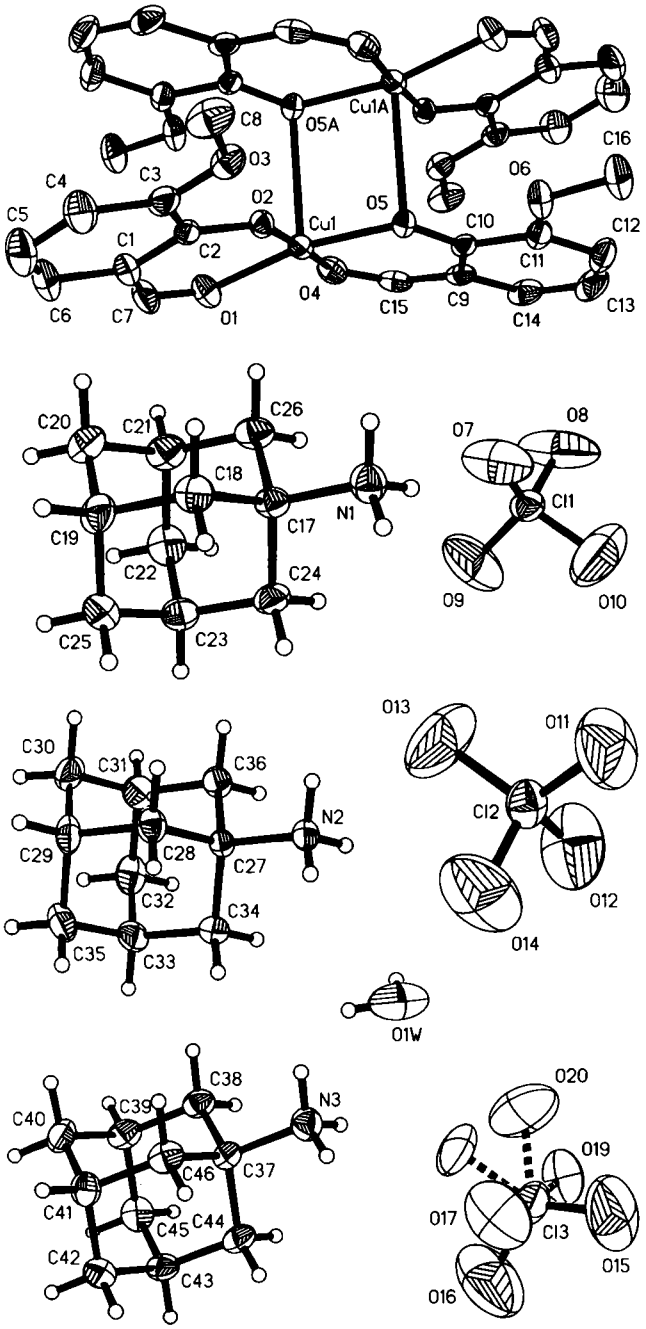

Abstract

$C_{92}H_{140}Cl_6Cu_2N_6O_{38}$, triclinic, $P\bar{1}$ (no. 2), a = 12.819(3) Å, b = 13.240(3) Å, c = 16.721(3) Å, α = 95.25(3)°, β = 103.27(3)°, γ = 106.01(3)°, V = 2618.5 Å^3, Z = 1, $R_{gt}(F)$ = 0.071, $wR_{ref}(F^2)$ = 0.220, T = 293 K.

Source of material

The title compound was synthesized by addition of copper(II) perchlorate hexahydrate (2.0 mmol) to an ethanol solution (20 ml) of adamantaneamine (1.0 mmol) with stirring for 1 hour. The solution was allowed to evaporation at room temperature, and green prismatic crystals suitable for X-ray structure determination were obtained after about seven days.

Experimental details

The water H atoms were refined freely due to their importance in the hydrogen bonding.

Discussion

The title crystal structure consists of a neutral Cu_2(*o*-vanillin)$_4$ complex, six adamantaneamine perchlorate units and two free water molecules. In the dinuclear Cu_2(*o*-vanillin)$_4$ unit, the two Cu atoms are bridged by two hydroxyl groups of two different *o*-vanillin ligands forming a four-member ring Cu_2O_2 core with the Cu···Cu distance being 3.318(1) Å and the center of the core corresponds to a crystallographic center of symmetry (figure, top). Each Cu(II) atom displays a distorted square-pyramidal environment. The basal plane of the complex is defined by atoms O1, O2, O4 and O5 (the r.m.s. deviation for the four ligating atoms is 0.09 Å and the deviation of atom Cu from the mean plane is 0.1052(3) Å). Atoms O5A (symmetry code: $-x,-y,1-z$) occupy the apical sites. The Cu1—O5A bond distances (2.242(3) Å) are longer than the Cu1—O distance (1.898(3) Å – 1.933(3) Å) in the basal plane, but shorter than the corresponding distances of 2.644(6) Å in the similar dinuclear bis(2,2′-bipyridyl)bis(3-methoxysalicylaldehydato)dicopper(II) complex [1]. In the adamantylammonium ion, the three six-member rings are in chair conformation with C—C distances in the range of 1.512(2) Å – 1.532(2) Å. Each C atom adopts the sp^3 hybrid, and the angles of the C–C–C are in the range of 108.3(2)° – 110.0(2)°. Atoms O17, O18, O19 and O20 in one perchlorato group are disordered (figure, bottom right) and the final occupancy factors for them are all 0.50. A 2D supramolecular network parallel to (001) is formed by intermolecular O–H···O and N–H···O hydrogen bond interactions.

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Table 1. Data collection and handling.

Crystal:	green prism, size 0.18 × 0.24 × 0.32 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.46 cm^{-1}
Diffractometer, scan mode:	Riguku R-axis RAPID, ω
$2\theta_{max}$:	54.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19305, 11737
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7227
$N(param)_{refined}$:	673
Programs:	SHELXS-97 [2], SHELXL-97 [3]

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

Atom	Site	x	y	z	U_{iso}
H(1WA)	2*i*	0.224(6)	0.784(3)	0.446(5)	0.123
H(1WB)	2*i*	0.169(3)	0.683(4)	0.423(5)	0.123
H(1A)	2*i*	0.4574	0.3189	0.1973	0.085
H(1B)	2*i*	0.4559	0.2073	0.1956	0.085
H(1C)	2*i*	0.5638	0.2932	0.2193	0.085
H(2A)	2*i*	−0.0910	0.2041	0.3397	0.058
H(2B)	2*i*	−0.0933	0.0927	0.3413	0.058
H(2C)	2*i*	0.0149	0.1781	0.3644	0.058
H(3A)	2*i*	0.2430	0.6487	0.2497	0.076
H(3B)	2*i*	0.2490	0.7617	0.2551	0.076
H(3C)	2*i*	0.2113	0.7007	0.3179	0.076
H(4)	2*i*	0.3740	0.4168	0.4324	0.101
H(5)	2*i*	0.5242	0.3443	0.4473	0.141
H(6)	2*i*	0.4966	0.1661	0.4548	0.111
H(7)	2*i*	0.3784	−0.0028	0.4540	0.083
H(8A)	2*i*	0.1063	0.4360	0.4208	0.119
H(8B)	2*i*	0.2295	0.4643	0.4777	0.119
H(8C)	2*i*	0.2069	0.4451	0.3805	0.119
H(12)	2*i*	−0.4350	−0.1700	0.2975	0.085
H(13)	2*i*	−0.4298	−0.3460	0.3048	0.100
H(14)	2*i*	−0.2653	−0.3777	0.3662	0.079
H(15)	2*i*	−0.0739	−0.3177	0.4354	0.062
H(16A)	2*i*	−0.3469	0.1071	0.3268	0.119
H(16B)	2*i*	−0.4007	−0.0030	0.2673	0.119
H(16C)	2*i*	−0.4099	0.0068	0.3593	0.119
H(18A)	2*i*	0.6344	0.3953	0.1193	0.064
H(18B)	2*i*	0.5218	0.4224	0.0945	0.064

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(19)	2*i*	0.6044	0.4332	−0.0179	0.070
H(20A)	2*i*	0.6998	0.3087	0.0069	0.079
H(20B)	2*i*	0.6265	0.2806	−0.0849	0.079
H(21)	2*i*	0.6003	0.1258	−0.0232	0.076
H(22A)	2*i*	0.4021	0.0710	−0.0605	0.084
H(22B)	2*i*	0.4443	0.1364	−0.1258	0.084
H(23)	2*i*	0.3076	0.1973	−0.0855	0.075
H(24A)	2*i*	0.3387	0.2768	0.0525	0.067
H(24B)	2*i*	0.3369	0.1585	0.0511	0.067
H(25A)	2*i*	0.4463	0.3262	−0.1218	0.077
H(25B)	2*i*	0.4068	0.3803	−0.0525	0.077
H(26A)	2*i*	0.5178	0.1149	0.0883	0.066
H(26B)	2*i*	0.6326	0.2054	0.1160	0.066
H(28A)	2*i*	0.0875	0.2759	0.2618	0.052
H(28B)	2*i*	−0.0254	0.3021	0.2350	0.052
H(29)	2*i*	0.0582	0.3073	0.1227	0.063
H(30A)	2*i*	0.1523	0.1815	0.1560	0.070
H(30B)	2*i*	0.0836	0.1518	0.0630	0.070
H(31)	2*i*	0.0516	0.0012	0.1255	0.063
H(32A)	2*i*	−0.1453	−0.0531	0.0894	0.068
H(32B)	2*i*	−0.1027	0.0072	0.0217	0.068
H(33)	2*i*	−0.2400	0.0728	0.0586	0.060
H(34A)	2*i*	−0.2092	0.1563	0.1954	0.052
H(34B)	2*i*	−0.2116	0.0383	0.1967	0.052
H(35A)	2*i*	−0.1001	0.1961	0.0201	0.068
H(35B)	2*i*	−0.1400	0.2538	0.0870	0.068
H(36A)	2*i*	−0.0305	−0.0053	0.2377	0.053
H(36B)	2*i*	0.0843	0.0850	0.2629	0.053
H(38A)	2*i*	0.0770	0.8176	0.2267	0.057
H(38B)	2*i*	0.0383	0.7535	0.2940	0.057
H(39)	2*i*	−0.1200	0.7685	0.1986	0.063
H(40A)	2*i*	−0.2258	0.5881	0.1606	0.066
H(40B)	2*i*	−0.1527	0.6094	0.2522	0.066
H(41)	2*i*	−0.1356	0.4570	0.1801	0.060
H(42A)	2*i*	−0.1714	0.5030	0.0460	0.064
H(42B)	2*i*	−0.0611	0.4713	0.0637	0.064
H(43)	2*i*	−0.0299	0.6310	0.0096	0.058
H(44A)	2*i*	0.1268	0.6119	0.1045	0.058
H(44B)	2*i*	0.1333	0.7316	0.1123	0.058
H(45A)	2*i*	−0.0440	0.7834	0.0830	0.068
H(45B)	2*i*	−0.1606	0.6956	0.0568	0.068
H(46A)	2*i*	0.0291	0.5586	0.2826	0.058
H(46B)	2*i*	0.0628	0.5056	0.2096	0.058

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*		0.07905(4)	−0.03411(4)	0.44311(3)	0.0383(3)	0.0449(3)	0.0376(3)	0.0164(2)	0.0127(2)	0.0100(2)
Cl(1)	2*i*		0.3276(1)	−0.0225(1)	0.20974(8)	0.0449(6)	0.0558(7)	0.0679(7)	0.0117(5)	0.0149(5)	0.0183(6)
Cl(2)	2*i*		0.2138(1)	0.62791(9)	0.64106(6)	0.0648(7)	0.0489(7)	0.0487(6)	0.0240(6)	0.0229(5)	0.0093(5)
Cl(3)	2*i*		0.3331(1)	0.4794(1)	0.20660(9)	0.0537(7)	0.0592(8)	0.0901(9)	0.0129(6)	0.0338(7)	0.0062(7)
O(1)	2*i*		0.2259(3)	−0.0516(3)	0.4520(2)	0.051(2)	0.074(2)	0.076(2)	0.031(2)	0.025(2)	0.021(2)
O(2)	2*i*		0.1309(2)	0.1108(2)	0.4305(2)	0.034(1)	0.048(2)	0.038(1)	0.005(1)	0.012(1)	0.010(1)
O(3)	2*i*		0.1640(3)	0.3119(3)	0.4261(2)	0.060(2)	0.046(2)	0.052(2)	0.001(2)	0.014(2)	0.010(1)
O(4)	2*i*		0.0327(3)	−0.1824(3)	0.4554(2)	0.060(2)	0.047(2)	0.061(2)	0.024(2)	0.026(2)	0.015(2)
O(5)	2*i*		−0.0734(2)	−0.0310(2)	0.4104(2)	0.033(1)	0.040(2)	0.041(1)	0.007(1)	0.007(1)	0.009(1)
O(6)	2*i*		−0.2605(2)	0.0067(3)	0.3494(2)	0.034(2)	0.072(2)	0.072(2)	0.014(2)	0.010(1)	0.027(2)
O(7)	2*i*		0.4178(4)	0.0668(5)	0.2301(5)	0.085(4)	0.101(4)	0.265(8)	−0.014(3)	−0.012(4)	0.113(5)
O(8)	2*i*		0.3602(5)	−0.1055(5)	0.2393(5)	0.088(4)	0.091(4)	0.34(1)	−0.002(3)	−0.044(5)	0.107(5)
O(9)	2*i*		0.2654(7)	−0.0457(6)	0.1281(4)	0.221(8)	0.213(8)	0.085(4)	0.079(6)	−0.030(4)	0.004(4)
O(10)	2*i*		0.2498(6)	−0.0144(8)	0.2510(5)	0.128(5)	0.28(1)	0.184(7)	0.040(6)	0.086(5)	−0.023(6)
O(11)	2*i*		0.2587(5)	0.6728(5)	0.7250(3)	0.154(5)	0.159(6)	0.066(3)	0.006(4)	0.018(3)	−0.009(3)
O(12)	2*i*		0.1423(6)	0.5242(4)	0.6302(4)	0.188(6)	0.072(4)	0.130(4)	−0.016(4)	0.046(4)	0.013(3)
O(13)	2*i*		0.2941(5)	0.6333(6)	0.5979(4)	0.118(4)	0.192(7)	0.152(5)	0.033(4)	0.090(4)	−0.012(4)
O(14)	2*i*		0.1484(6)	0.6874(6)	0.6025(4)	0.209(7)	0.166(6)	0.135(5)	0.139(6)	0.031(4)	0.034(4)
O(15)	2*i*		0.4347(5)	0.4673(6)	0.2262(6)	0.093(4)	0.183(7)	0.31(1)	0.065(5)	0.003(5)	−0.104(7)
O(16)	2*i*		0.2704(7)	0.4500(7)	0.1221(4)	0.185(7)	0.25(1)	0.113(5)	−0.021(7)	−0.019(5)	0.044(5)
O(17)	2*i*	0.5	0.306(1)	0.3690(8)	0.2245(8)	0.16(1)	0.065(7)	0.15(1)	0.011(7)	0.019(8)	0.031(6)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(18)	2*i*	0.5	0.2472(8)	0.457(1)	0.2450(7)	0.077(6)	0.117(9)	0.123(8)	0.005(6)	0.069(6)	0.014(7)
O(19)	2*i*	0.5	0.3638(7)	0.5928(6)	0.2043(6)	0.071(5)	0.057(5)	0.115(7)	0.012(4)	0.012(5)	0.032(5)
O(20)	2*i*	0.5	0.329(1)	0.537(1)	0.2795(9)	0.20(2)	0.14(1)	0.16(1)	0.09(1)	0.09(1)	0.00(1)
O(1W)	2*i*		0.2337(5)	0.7260(5)	0.4360(3)	0.152(5)	0.127(4)	0.063(3)	0.091(4)	0.033(3)	0.022(3)
N(1)	2*i*		0.4929(3)	0.2716(3)	0.1862(2)	0.065(3)	0.051(2)	0.059(2)	0.019(2)	0.020(2)	0.016(2)
N(2)	2*i*		−0.0555(3)	0.1560(3)	0.3306(2)	0.042(2)	0.043(2)	0.035(2)	0.015(2)	0.014(1)	0.011(1)
N(3)	2*i*		0.2106(3)	0.6975(3)	0.2638(2)	0.048(2)	0.052(2)	0.050(2)	0.011(2)	0.013(2)	0.011(2)
C(1)	2*i*		0.3263(4)	0.1270(5)	0.4466(3)	0.040(2)	0.071(4)	0.070(3)	0.008(2)	0.023(2)	0.002(3)
C(2)	2*i*		0.2338(3)	0.1684(4)	0.4371(2)	0.038(2)	0.061(3)	0.028(2)	0.001(2)	0.013(2)	0.001(2)
C(3)	2*i*		0.2548(4)	0.2784(4)	0.4338(3)	0.056(3)	0.057(3)	0.041(2)	−0.002(2)	0.017(2)	0.000(2)
C(4)	2*i*		0.3610(5)	0.3426(5)	0.4360(4)	0.066(4)	0.075(4)	0.100(4)	−0.011(3)	0.041(3)	0.010(3)
C(5)	2*i*		0.4501(6)	0.2993(7)	0.4447(5)	0.063(4)	0.112(7)	0.152(7)	−0.024(4)	0.052(4)	−0.010(5)
C(6)	2*i*		0.4345(5)	0.1945(6)	0.4494(4)	0.042(3)	0.109(6)	0.120(5)	0.011(3)	0.032(3)	−0.003(4)
C(7)	2*i*		0.3124(4)	0.0191(5)	0.4513(3)	0.041(3)	0.100(5)	0.076(3)	0.032(3)	0.020(2)	0.013(3)
C(8)	2*i*		0.1778(6)	0.4237(4)	0.4265(3)	0.110(5)	0.045(3)	0.072(3)	0.006(3)	0.025(3)	0.008(3)
C(9)	2*i*		−0.1630(4)	−0.2210(4)	0.3896(2)	0.059(3)	0.045(3)	0.034(2)	0.006(2)	0.021(2)	−0.001(2)
C(10)	2*i*		−0.1625(3)	−0.1154(3)	0.3839(2)	0.039(2)	0.046(2)	0.027(2)	0.001(2)	0.013(2)	0.003(2)
C(11)	2*i*		−0.2674(4)	−0.0981(4)	0.3492(2)	0.039(2)	0.066(3)	0.036(2)	0.003(2)	0.009(2)	0.013(2)
C(12)	2*i*		−0.3649(4)	−0.1827(5)	0.3204(3)	0.042(3)	0.095(5)	0.050(3)	−0.007(3)	0.002(2)	0.008(3)
C(13)	2*i*		−0.3619(5)	−0.2874(5)	0.3262(3)	0.066(4)	0.081(5)	0.064(3)	−0.028(3)	0.012(3)	−0.013(3)
C(14)	2*i*		−0.2656(5)	−0.3062(4)	0.3609(3)	0.080(4)	0.042(3)	0.058(3)	−0.012(3)	0.027(3)	−0.010(2)
C(15)	2*i*		−0.0645(5)	−0.2449(4)	0.4284(3)	0.081(3)	0.041(3)	0.047(2)	0.021(3)	0.037(2)	0.009(2)
C(16)	2*i*		−0.3628(4)	0.0314(5)	0.3236(4)	0.043(3)	0.104(5)	0.097(4)	0.030(3)	0.014(3)	0.035(4)
C(17)	2*i*		0.4968(3)	0.2636(3)	0.0970(3)	0.040(2)	0.036(2)	0.055(2)	0.013(2)	0.010(2)	0.010(2)
C(18)	2*i*		0.5597(4)	0.3719(4)	0.0826(3)	0.051(3)	0.036(2)	0.066(3)	0.007(2)	0.011(2)	0.010(2)
C(19)	2*i*		0.5641(4)	0.3646(4)	−0.0085(3)	0.053(3)	0.046(3)	0.076(3)	0.006(2)	0.025(2)	0.020(2)
C(20)	2*i*		0.6238(4)	0.2855(4)	−0.0278(4)	0.049(3)	0.071(4)	0.079(3)	0.014(3)	0.023(2)	0.013(3)
C(21)	2*i*		0.5623(4)	0.1760(4)	−0.0109(3)	0.065(3)	0.055(3)	0.081(3)	0.031(3)	0.023(3)	0.009(3)
C(22)	2*i*		0.4420(5)	0.1404(4)	−0.0687(3)	0.075(4)	0.056(3)	0.066(3)	0.008(3)	0.014(3)	0.000(3)
C(23)	2*i*		0.3828(4)	0.2207(4)	−0.0495(3)	0.040(2)	0.073(4)	0.062(3)	0.007(2)	0.002(2)	0.012(3)
C(24)	2*i*		0.3772(4)	0.2267(4)	0.0410(3)	0.034(2)	0.056(3)	0.075(3)	0.011(2)	0.014(2)	0.020(2)
C(25)	2*i*		0.4449(4)	0.3300(4)	−0.0644(3)	0.063(3)	0.068(4)	0.065(3)	0.024(3)	0.015(2)	0.026(3)
C(26)	2*i*		0.5580(4)	0.1837(4)	0.0792(3)	0.052(3)	0.042(3)	0.074(3)	0.023(2)	0.013(2)	0.012(2)
C(27)	2*i*		−0.0510(3)	0.1438(3)	0.2418(2)	0.036(2)	0.032(2)	0.029(2)	0.013(2)	0.011(1)	0.007(1)
C(28)	2*i*		0.0128(4)	0.2511(3)	0.2252(2)	0.048(2)	0.038(2)	0.040(2)	0.007(2)	0.011(2)	0.008(2)
C(29)	2*i*		0.0176(4)	0.2402(4)	0.1343(2)	0.060(3)	0.051(3)	0.038(2)	−0.001(2)	0.015(2)	0.017(2)
C(30)	2*i*		0.0776(4)	0.1583(4)	0.1194(3)	0.047(3)	0.086(4)	0.040(2)	0.012(3)	0.019(2)	0.009(2)
C(31)	2*i*		0.0134(4)	0.0519(4)	0.1361(3)	0.063(3)	0.062(3)	0.044(2)	0.032(2)	0.021(2)	0.006(2)
C(32)	2*i*		−0.1052(4)	0.0149(4)	0.0788(3)	0.074(3)	0.051(3)	0.039(2)	0.008(2)	0.020(2)	−0.004(2)
C(33)	2*i*		−0.1650(4)	0.0963(4)	0.0949(2)	0.042(2)	0.061(3)	0.034(2)	0.007(2)	−0.001(2)	0.008(2)
C(34)	2*i*		−0.1708(3)	0.1056(4)	0.1854(2)	0.037(2)	0.050(3)	0.042(2)	0.014(2)	0.008(2)	0.009(2)
C(35)	2*i*		−0.1020(4)	0.2026(4)	0.0773(3)	0.067(3)	0.060(3)	0.040(2)	0.016(3)	0.008(2)	0.020(2)
C(36)	2*i*		0.0094(4)	0.0624(4)	0.2266(2)	0.054(2)	0.049(3)	0.043(2)	0.030(2)	0.019(2)	0.013(2)
C(37)	2*i*		0.0910(3)	0.6662(3)	0.2115(2)	0.041(2)	0.039(2)	0.040(2)	0.013(2)	0.016(2)	0.009(2)
C(38)	2*i*		0.0364(4)	0.7490(3)	0.2360(3)	0.059(3)	0.039(2)	0.050(2)	0.016(2)	0.023(2)	0.004(2)
C(39)	2*i*		−0.0846(4)	0.7174(4)	0.1830(3)	0.062(3)	0.047(3)	0.060(3)	0.030(2)	0.026(2)	0.004(2)
C(40)	2*i*		−0.1500(4)	0.6076(4)	0.1951(3)	0.047(3)	0.060(3)	0.061(3)	0.013(2)	0.027(2)	0.011(2)
C(41)	2*i*		−0.0945(4)	0.5258(4)	0.1715(3)	0.051(3)	0.039(2)	0.055(2)	0.003(2)	0.018(2)	0.011(2)
C(42)	2*i*		−0.0951(4)	0.5232(4)	0.0799(3)	0.056(3)	0.046(3)	0.052(2)	0.009(2)	0.014(2)	−0.003(2)
C(43)	2*i*		−0.0298(4)	0.6334(4)	0.0671(2)	0.061(3)	0.054(3)	0.034(2)	0.017(2)	0.018(2)	0.012(2)
C(44)	2*i*		0.0914(4)	0.6628(4)	0.1202(2)	0.058(3)	0.051(3)	0.044(2)	0.017(2)	0.027(2)	0.014(2)
C(45)	2*i*		−0.0846(4)	0.7142(4)	0.0911(3)	0.060(3)	0.055(3)	0.058(3)	0.021(2)	0.013(2)	0.024(2)

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