Electronic Supplementary Material (ESI) for Dalton Transactions

Doubly Phenoxo/Hydroxo-bridged Dicopper(II) Complexes: Individual Contributions of the Bridges to Antiferromagnetic Coupling Based on two Related Biomimetic Models for Catechol Oxidases

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Electronic supplementary information of crystallographic analysis of complex **2**.

X-ray crystallography:

Crystals of complex **2** were grown by slow evaporation of a MeCN solution. A dark-green crystal with dimensions of 0.50 x 0.40 x 0.13 mm^3 was selected for crystallographic analysis, which was carried out on a CAD-4 Enraf–Nonius diffractometer using graphite monochromated Mo-K_α radiation (λ =0.71073 Å), at room temperature. Cell parameters were determined from 25 centered reflections in the θ range of 6.88–13.47^o. 5829 reflections were collected using ω-2θ scan technique. Intensity was controlled from three standard reflections, which were monitored at regular intervals, and no significant loss of intensity was observed during the data collection. The collected intensities were corrected for the Lorentz and for polarization effects.[1] All measured intensities were also corrected for absorption effect using semi-empirical Ψ-scan method.[2] The structure was solved by direct methods and was refined by the full-matrix least-squares method using the SIR97[3] and SHELXL[4] software, respectively. Disordered oxygen atoms of the second perchlorate anion were refined isotropically, whereas other non-hydrogen atoms were refined with anisotropic displacement parameters. Three oxygen atoms of the perchlorate anions are disordered over two alternative positions and their occupancy factors were refined. Hydrogen atoms bonded to C atoms were placed at their idealized positions using standard geometric criteria. H atoms of the hydroxo-bridge and secondary amine groups

were located from Fourier difference map and treated with riding model. ORTEP plot of the cation complex was drawn with the PLATON software.[2(a)]

References:

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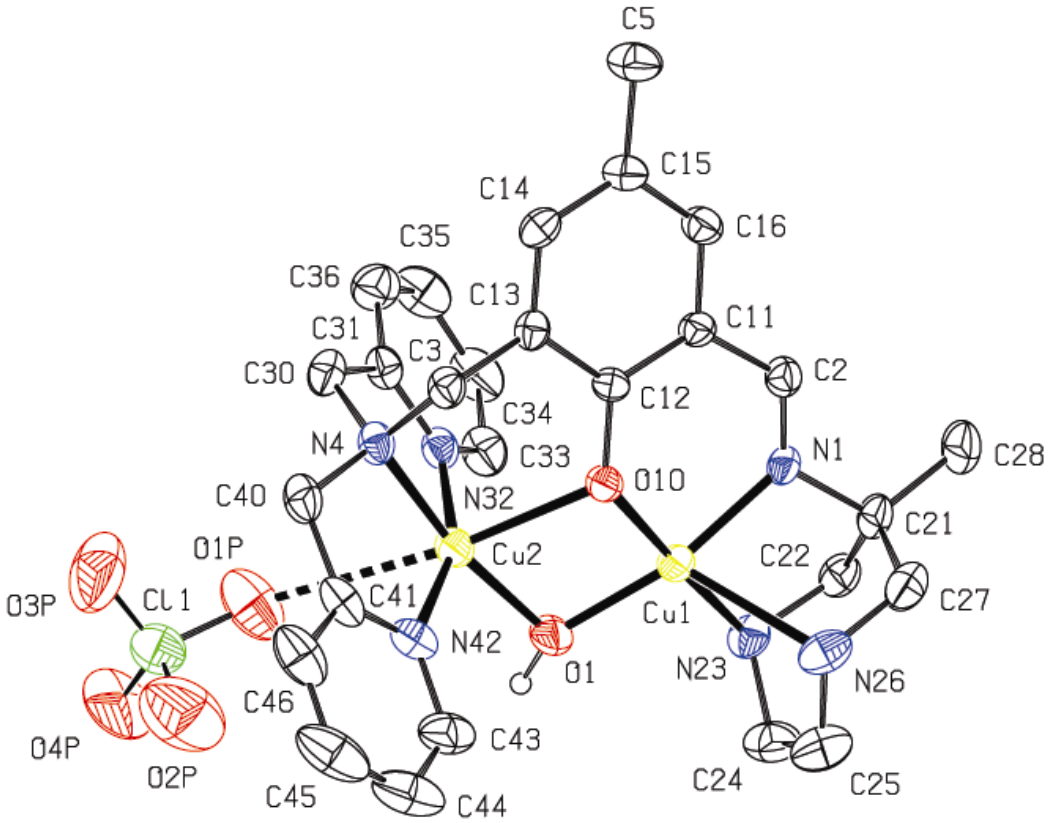

Figure 1. ORTEP plot of the cation complex $[Cu_2(\mu\text{-}OH)(L2)(ClO_4)]^+$.

Table 1. Crystal data and structure refinement for complex **2**.

Empirical formula	$C_{27}H_{34}Cl_2Cu_2N_6O_{10}$
Formula weight	800.58
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 16.607(1) Å
	b = 11.022(2) Å
	c = 17.330(1) Å
	β= 91.561(5)°
Volume	3170.9(6) $Å^3$
Z	4
Density (calculated)	1.677 Mg/m^3
Absorption coefficient	1.576 mm^{-1}
F(000)	1640
Crystal size	0.50 x 0.40 x 0.13 mm^3
Theta range for data collection	1.68 to 25.07°.
Index ranges	$-19 \le h \le 19$, $-13 \le k \le 0$, $-20 \le l \le 0$
Reflections collected	5829
Independent reflections	5633 (R_{int} = 0.0263)
Absorption correction	Psi-scan
Max. and min. transmission	0.8214 and 0.5063
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5633 / 177 / 451
Goodness-of-fit on F^2	1.065
Final R indices [I>2σ(I)]	R_1 = 0.0508, wR_2 = 0.1268
R indices (all data)	R_1 = 0.1118, wR_2 = 0.1449
Largest diff. peak and hole	0.805 and -0.664 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for complex **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu1	1553(1)	3876(1)	10204(1)	34(1)
Cu2	2468(1)	5468(1)	9104(1)	38(1)
O1	2117(3)	3816(4)	9250(3)	47(1)
O10	1550(3)	5621(4)	10040(2)	34(1)
N1	1242(3)	4079(5)	11265(3)	33(1)
C2	1256(4)	5041(6)	11659(4)	36(2)
C3	2030(4)	7923(6)	9552(3)	37(2)
N4	2666(3)	7286(5)	9093(3)	36(1)
C5	2017(5)	9253(6)	12332(4)	53(2)
C11	1545(4)	6206(5)	11384(3)	32(1)
C12	1696(4)	6431(5)	10591(3)	29(1)
C13	1969(4)	7604(5)	10390(3)	31(1)
C14	2093(4)	8466(6)	10956(4)	38(2)
C15	1929(4)	8269(6)	11734(4)	38(2)
C16	1654(4)	7138(6)	11927(4)	39(2)
C21	867(4)	2933(6)	11524(4)	40(2)
C22	1432(4)	1931(6)	11270(4)	41(2)
N23	1639(3)	2071(5)	10443(3)	40(1)
C24	1115(5)	1352(7)	9906(5)	61(2)
C25	264(5)	1854(8)	9841(5)	70(2)
N26	167(4)	3002(5)	10247(4)	50(2)
C27	64(4)	2885(7)	11073(4)	52(2)
C28	740(5)	2830(7)	12389(4)	61(2)
C30	3483(4)	7538(6)	9423(4)	44(2)
C31	3743(4)	6542(6)	9976(4)	37(2)
N32	3393(3)	5461(5)	9861(3)	37(1)
C33	3660(5)	4525(7)	10289(4)	49(2)
C34	4260(5)	4634(8)	10846(4)	57(2)
C35	4593(5)	5746(8)	10974(4)	59(2)
C36	4334(4)	6719(8)	10540(4)	53(2)
C40	2571(4)	7692(6)	8278(4)	46(2)

C41	1975(4)	6900(7)	7834(4)	49(2)
N42	1850(3)	5794(5)	8127(3)	45(1)
C43	1375(5)	5016(8)	7728(5)	58(2)
C44	1016(6)	5313(10)	7024(5)	77(3)
C45	1162(6)	6466(11)	6727(5)	85(3)
C46	1636(5)	7282(10)	7138(5)	70(3)
Cl1	4083(1)	5707(2)	7270(1)	62(1)
O1P	3837(4)	5398(6)	8029(3)	94(2)
O2P	3357(8)	5700(30)	6823(9)	141(8)
O2P'	3676(17)	4920(19)	6738(8)	131(9)
O3P	4394(15)	6858(14)	7314(12)	143(10)
O3P'	3886(15)	6888(12)	7047(11)	99(8)
O4P	4590(14)	4891(15)	6972(10)	117(8)
O4P'	4917(8)	5510(30)	7218(12)	129(9)
Cl2	1116(1)	5928(2)	4288(1)	54(1)
O5P	1620(4)	6691(7)	3862(4)	111(3)
O6P	954(7)	4928(11)	3813(7)	110(5)
O6P'	1019(12)	4700(12)	4104(14)	72(8)
O7P	1651(6)	5611(10)	4939(5)	84(4)
O7P'	1395(15)	5980(30)	5075(9)	220(20)
O8P	461(6)	6500(10)	4586(8)	109(5)
O8P'	332(9)	6494(17)	4224(16)	88(9)

Table 3. Selected bond lengths [Å] and angles [°] for complex **2**.

Cu1-O1	1.923(4)	Cu2-O1	1.930(5)
Cu1-N1	1.936(5)	Cu2-N42	1.989(6)
Cu1-O10	1.944(4)	Cu2-N32	1.994(5)
Cu1-N23	2.036(5)	Cu2-N4	2.032(5)
Cu1-N26	2.498(6)	Cu2-O10	2.262(4)
Cu1-Cu2	3.0302(11)	Cu2-O1P	2.979(6)
O1-Cu1-N1	165.7(2)	N32-Cu2-N4	83.5(2)
O1-Cu1-O10	84.65(18)	O1-Cu2-O10	76.37(17)
N1-Cu1-O10	91.46(19)	N42-Cu2-O10	104.8(2)
O1-Cu1-N23	96.2(2)	N32-Cu2-O10	92.87(18)
N1-Cu1-N23	86.5(2)	N4-Cu2-O10	92.62(18)
O10-Cu1-N23	175.0(2)	O1-Cu2-O1P	107.23(19)
O1-Cu1-N26	118.9(2)	N42-Cu2-O1P	81.8(2)
N1-Cu1-N26	75.3(2)	N32-Cu2-O1P	79.88(19)
O10-Cu1-N26	112.79(19)	N4-Cu2-O1P	83.9(2)
N23-Cu1-N26	71.2(2)	O10-Cu2-O1P	172.23(17)
O1-Cu2-N42	97.6(2)	Cu1-O1-Cu2	103.7(2)
O1-Cu2-N32	98.1(2)	C12-O10-Cu1	124.1(4)
N42-Cu2-N32	158.7(2)	C12-O10-Cu2	117.0(4)
O1-Cu2-N4	168.9(2)	Cu1-O10-Cu2	91.87(16)
N42-Cu2-N4	83.9(2)		

Table 4. Bond lengths [Å] and angles [°] for complex **2**.

Cu(1)-O(1)	1.923(4)	N(26)-C(27)	1.452(9)
Cu(1)-N(1)	1.936(5)	C(30)-C(31)	1.513(9)
Cu(1)-O(10)	1.944(4)	C(31)-N(32)	1.338(8)
Cu(1)-N(23)	2.036(5)	C(31)-C(36)	1.379(9)
Cu(1)-N(26)	2.498(6)	N(32)-C(33)	1.339(8)
Cu(1)-Cu(2)	3.0302(11)	C(33)-C(34)	1.374(10)
Cu(2)-O(1)	1.930(5)	C(34)-C(35)	1.360(11)
Cu(2)-N(42)	1.989(6)	C(35)-C(36)	1.373(11)
Cu(2)-N(32)	1.994(5)	C(40)-C(41)	1.514(10)
Cu(2)-N(4)	2.032(5)	C(41)-N(42)	1.338(9)
Cu(2)-O(10)	2.262(4)	C(41)-C(46)	1.383(10)
Cu(2)-O(1P)	2.979(6)	N(42)-C(43)	1.344(9)
O(10)-C(12)	1.325(7)	C(43)-C(44)	1.383(11)
N(1)-C(2)	1.260(8)	C(44)-C(45)	1.395(14)
N(1)-C(21)	1.483(8)	C(45)-C(46)	1.381(13)
C(2)-C(11)	1.456(8)	Cl(1)-O(4P)	1.345(10)
C(3)-C(13)	1.501(8)	Cl(1)-O(3P)	1.371(11)
C(3)-N(4)	1.512(8)	Cl(1)-O(3P')	1.394(10)
N(4)-C(30)	1.484(8)	Cl(1)-O(4P')	1.407(11)
N(4)-C(40)	1.485(8)	Cl(1)-O(2P)	1.415(11)
C(5)-C(15)	1.505(9)	Cl(1)-O(2P')	1.423(11)
C(11)-C(16)	1.401(8)	Cl(1)-O(1P)	1.430(6)
C(11)-C(12)	1.425(8)	O(2P)-O(2P')	1.025(18)
C(12)-C(13)	1.417(8)	O(2P)-O(3P')	1.62(2)
C(13)-C(14)	1.377(9)	O(2P')-O(4P)	1.56(2)
C(14)-C(15)	1.400(9)	O(3P)-O(3P')	0.951(18)
C(15)-C(16)	1.372(9)	O(3P)-O(4P')	1.73(2)
C(21)-C(22)	1.522(9)	O(4P)-O(4P')	0.967(18)
C(21)-C(28)	1.524(9)	Cl(2)-O(8P)	1.369(9)
C(21)-C(27)	1.529(10)	Cl(2)-O(6P')	1.399(12)
C(22)-N(23)	1.491(8)	Cl(2)-O(6P)	1.399(9)
N(23)-C(24)	1.486(9)	Cl(2)-O(5P)	1.410(6)
C(24)-C(25)	1.519(11)	Cl(2)-O(7P')	1.430(13)
C(25)-N(26)	1.458(10)	Cl(2)-O(8P')	1.445(13)

Cl(2)-O(7P)	1.460(8)	O(7P)-O(7P')	0.64(3)
O(6P)-O(6P')	0.57(2)	O(8P)-O(8P')	0.66(2)

O(1)-Cu(1)-N(1)	165.7(2)	C(13)-C(3)-N(4)	117.9(5)
O(1)-Cu(1)-O(10)	84.65(18)	C(30)-N(4)-C(40)	112.5(5)
N(1)-Cu(1)-O(10)	91.46(19)	C(30)-N(4)-C(3)	110.8(5)
O(1)-Cu(1)-N(23)	96.2(2)	C(40)-N(4)-C(3)	107.6(5)
N(1)-Cu(1)-N(23)	86.5(2)	C(30)-N(4)-Cu(2)	109.1(4)
O(10)-Cu(1)-N(23)	175.0(2)	C(40)-N(4)-Cu(2)	107.0(4)
O(1)-Cu(1)-N(26)	118.9(2)	C(3)-N(4)-Cu(2)	109.7(4)
N(1)-Cu(1)-N(26)	75.3(2)	C(16)-C(11)-C(12)	119.8(6)
O(10)-Cu(1)-N(26)	112.79(19)	C(16)-C(11)-C(2)	117.7(5)
N(23)-Cu(1)-N(26)	71.2(2)	C(12)-C(11)-C(2)	122.5(5)
O(1)-Cu(2)-N(42)	97.6(2)	O(10)-C(12)-C(13)	119.4(5)
O(1)-Cu(2)-N(32)	98.1(2)	O(10)-C(12)-C(11)	123.0(5)
N(42)-Cu(2)-N(32)	158.7(2)	C(13)-C(12)-C(11)	117.5(5)
O(1)-Cu(2)-N(4)	168.9(2)	C(14)-C(13)-C(12)	119.8(6)
N(42)-Cu(2)-N(4)	83.9(2)	C(14)-C(13)-C(3)	121.0(6)
N(32)-Cu(2)-N(4)	83.5(2)	C(12)-C(13)-C(3)	118.8(5)
O(1)-Cu(2)-O(10)	76.37(17)	C(13)-C(14)-C(15)	123.3(6)
N(42)-Cu(2)-O(10)	104.8(2)	C(16)-C(15)-C(14)	116.8(6)
N(32)-Cu(2)-O(10)	92.87(18)	C(16)-C(15)-C(5)	121.0(6)
N(4)-Cu(2)-O(10)	92.62(18)	C(14)-C(15)-C(5)	122.2(6)
O(1)-Cu(2)-O(1P)	107.23(19)	C(15)-C(16)-C(11)	122.7(6)
N(42)-Cu(2)-O(1P)	81.8(2)	N(1)-C(21)-C(22)	105.3(5)
N(32)-Cu(2)-O(1P)	79.88(19)	N(1)-C(21)-C(28)	115.6(6)
N(4)-Cu(2)-O(1P)	83.9(2)	C(22)-C(21)-C(28)	109.5(6)
O(10)-Cu(2)-O(1P)	172.23(17)	N(1)-C(21)-C(27)	104.0(5)
Cu(1)-O(1)-Cu(2)	103.7(2)	C(22)-C(21)-C(27)	111.3(6)
C(12)-O(10)-Cu(1)	124.1(4)	C(28)-C(21)-C(27)	110.9(6)
C(12)-O(10)-Cu(2)	117.0(4)	N(23)-C(22)-C(21)	111.3(5)
Cu(1)-O(10)-Cu(2)	91.87(16)	C(24)-N(23)-C(22)	113.6(6)
C(2)-N(1)-C(21)	123.7(5)	C(24)-N(23)-Cu(1)	110.9(4)
C(2)-N(1)-Cu(1)	127.6(4)	C(22)-N(23)-Cu(1)	106.2(4)
C(21)-N(1)-Cu(1)	108.3(4)	N(23)-C(24)-C(25)	112.3(6)
N(1)-C(2)-C(11)	124.5(6)	N(26)-C(25)-C(24)	113.3(6)

C(27)-N(26)-C(25)	114.6(6)	O(4P)-Cl(1)-O(3P)	113.7(9)
C(27)-N(26)-Cu(1)	101.3(4)	O(3P')-Cl(1)-O(4P')	110.3(8)
C(25)-N(26)-Cu(1)	101.9(5)	O(4P)-Cl(1)-O(2P)	108.7(8)
N(26)-C(27)-C(21)	112.1(6)	O(3P)-Cl(1)-O(2P)	110.4(8)
N(4)-C(30)-C(31)	110.6(5)	O(3P')-Cl(1)-O(2P')	106.6(8)
N(32)-C(31)-C(36)	121.9(6)	O(4P')-Cl(1)-O(2P')	108.5(8)
N(32)-C(31)-C(30)	115.9(6)	O(4P)-Cl(1)-O(1P)	113.1(7)
C(36)-C(31)-C(30)	122.1(7)	O(3P)-Cl(1)-O(1P)	106.6(8)
C(31)-N(32)-C(33)	117.9(6)	O(3P')-Cl(1)-O(1P)	114.0(7)
C(31)-N(32)-Cu(2)	114.7(4)	O(4P')-Cl(1)-O(1P)	109.2(8)
C(33)-N(32)-Cu(2)	127.2(5)	O(2P)-Cl(1)-O(1P)	104.0(7)
N(32)-C(33)-C(34)	123.0(7)	O(2P')-Cl(1)-O(1P)	108.0(7)
C(35)-C(34)-C(33)	118.5(7)	Cl(1)-O(1P)-Cu(2)	144.3(4)
C(34)-C(35)-C(36)	119.7(8)	O(8P)-Cl(2)-O(6P)	116.3(7)
C(35)-C(36)-C(31)	118.9(8)	O(6P')-Cl(2)-O(6P)	23.6(9)
N(4)-C(40)-C(41)	111.2(5)	O(8P)-Cl(2)-O(5P)	114.3(6)
N(42)-C(41)-C(46)	123.0(8)	O(6P')-Cl(2)-O(5P)	121.6(9)
N(42)-C(41)-C(40)	116.0(6)	O(6P)-Cl(2)-O(5P)	105.6(6)
C(46)-C(41)-C(40)	120.8(8)	O(6P')-Cl(2)-O(7P')	106.8(9)
C(41)-N(42)-C(43)	118.8(7)	O(5P)-Cl(2)-O(7P')	107.1(9)
C(41)-N(42)-Cu(2)	113.9(5)	O(6P')-Cl(2)-O(8P')	107.6(9)
C(43)-N(42)-Cu(2)	127.2(6)	O(5P)-Cl(2)-O(8P')	104.4(8)
N(42)-C(43)-C(44)	122.4(9)	O(7P')-Cl(2)-O(8P')	108.9(8)
C(43)-C(44)-C(45)	117.8(9)	O(8P)-Cl(2)-O(7P)	107.0(6)
C(46)-C(45)-C(44)	120.4(9)	O(6P)-Cl(2)-O(7P)	111.7(6)
C(45)-C(46)-C(41)	117.7(10)	O(5P)-Cl(2)-O(7P)	100.9(5)

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for complex **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	42(1)	27(1)	34(1)	1(1)	2(1)	-2(1)
Cu(2)	49(1)	31(1)	34(1)	1(1)	5(1)	1(1)
O(1)	66(3)	33(3)	44(3)	-9(2)	16(2)	-1(2)
O(10)	47(3)	26(2)	29(2)	2(2)	4(2)	-2(2)
N(1)	36(3)	29(3)	34(3)	5(2)	3(2)	-7(2)
C(2)	37(4)	37(4)	33(3)	4(3)	2(3)	-2(3)
C(3)	43(4)	30(3)	37(4)	6(3)	4(3)	1(3)
N(4)	41(3)	32(3)	35(3)	7(2)	6(2)	3(2)
C(5)	78(6)	38(4)	43(4)	-7(3)	-8(4)	3(4)
C(11)	41(4)	25(3)	30(3)	1(3)	0(3)	-3(3)
C(12)	30(3)	25(3)	30(3)	-3(3)	1(3)	4(3)
C(13)	31(3)	27(3)	36(3)	5(3)	3(3)	2(3)
C(14)	41(4)	25(3)	47(4)	3(3)	-1(3)	-2(3)
C(15)	44(4)	33(4)	35(4)	-5(3)	-5(3)	3(3)
C(16)	49(4)	36(4)	30(3)	-1(3)	1(3)	0(3)
C(21)	43(4)	35(4)	42(4)	10(3)	5(3)	-7(3)
C(22)	45(4)	31(4)	47(4)	7(3)	-1(3)	-3(3)
N(23)	46(3)	26(3)	50(3)	4(2)	3(3)	2(3)
C(24)	83(6)	40(4)	58(5)	-10(4)	-8(4)	-3(4)
C(25)	64(6)	66(6)	80(6)	-13(5)	-18(5)	-11(5)
N(26)	45(4)	39(3)	65(4)	0(3)	-16(3)	0(3)
C(27)	43(4)	46(4)	67(5)	1(4)	6(4)	-10(4)
C(28)	78(6)	51(5)	55(5)	12(4)	19(4)	-14(4)
C(30)	42(4)	38(4)	51(4)	6(3)	7(3)	-6(3)
C(31)	33(4)	45(4)	34(4)	3(3)	5(3)	2(3)
N(32)	42(3)	32(3)	37(3)	1(3)	11(2)	3(3)
C(33)	61(5)	39(4)	48(4)	8(3)	8(4)	9(4)
C(34)	67(5)	58(5)	45(4)	11(4)	-3(4)	23(5)
C(35)	61(5)	72(6)	45(5)	1(4)	-8(4)	20(5)
C(36)	43(4)	59(5)	56(5)	-5(4)	-2(4)	-1(4)
C(40)	55(5)	44(4)	39(4)	13(3)	9(3)	1(4)

C(41)	52(5)	64(5)	31(4)	3(4)	9(3)	16(4)
N(42)	47(3)	52(4)	34(3)	-7(3)	0(3)	9(3)
C(43)	58(5)	55(5)	60(5)	-23(4)	1(4)	10(4)
C(44)	69(6)	98(8)	62(6)	-37(6)	-17(5)	33(6)
C(45)	79(7)	126(10)	48(5)	-19(6)	-16(5)	51(7)
C(46)	70(6)	98(7)	41(5)	12(5)	6(4)	26(5)
Cl(1)	68(1)	64(1)	55(1)	-1(1)	-4(1)	8(1)
O(1P)	110(5)	110(6)	62(4)	16(4)	14(4)	38(5)
O(2P)	131(14)	200(20)	94(11)	-14(14)	-23(10)	29(15)
O(2P')	210(20)	88(14)	89(11)	9(10)	-51(13)	-73(14)
O(3P)	160(20)	68(12)	210(20)	-23(12)	107(17)	-29(12)
O(3P')	161(19)	39(8)	100(12)	20(8)	64(13)	35(10)
O(4P)	153(17)	78(11)	121(13)	-28(9)	63(13)	45(11)
O(4P')	85(12)	160(20)	150(18)	26(16)	48(12)	25(14)
Cl(2)	57(1)	48(1)	57(1)	-4(1)	13(1)	5(1)
O(5P)	100(6)	143(7)	91(5)	21(5)	25(4)	-33(5)

Table 6. Hydrogen bonds for complex **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N23-H23...O5P^{i}	0.98	2.34	3.129(9)	136
N23-H23...O7P^{i}	0.98	2.38	3.345(11)	166
N23-H23...O7P'^{i}	0.98	2.65	3.62(2)	169
N26-H26...O10^{ii}	0.91	2.48	3.256(7)	144

Symmetry transformations used to generate equivalent atoms:

(i) -x+1/2,y-1/2,-z+3/2 (ii) -x,-y+1,-z+2