## **Electronic Supplementary Information (ESI)**

# Identification of potent anticancer copper(II) complexes containing tripodal bis[2-ethyl-di(3,5-dialkyl-1*H*-pyrazol-1yl)]amine moiety†

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### X-ray crystal structure analysis

The X-ray single-crystal data of compounds were collected on a Bruker-AXS APEX-II CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table S1. The intensities were collected with Mo-K $\alpha$  radiation ( $\lambda$ = 0.71073 Å). Data processing, Lorentz-polarization and absorption corrections were performed using SAINT, APEX and the SADABS computer programs.<sup>S1</sup> The structures were solved by direct methods and refined by full-matrix least-squares methods on F<sup>2</sup>, using the SHELX program package.<sup>S2</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. Further programs used: Mercury [S3],<sup>S3</sup> Olex<sup>S4</sup> and Platon.<sup>S5</sup>

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- S4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann *J. Appl. Cryst.* 2009, **42**, 339-341.
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Compound	1-ClO <sub>4</sub>	2-ClO <sub>4</sub>	4-ClO <sub>4</sub>	5-PF <sub>6</sub>
Empirical formula	$C_{21.5}H_{32}Cl_2CuN_6O_{4.5}$	$C_{22}H_{32}Cl_2CuN_6O_6$	$C_{20}H_{31}Cl_2CuN_7O_4$	C <sub>25</sub> H <sub>33</sub> ClCuF <sub>6</sub> N <sub>7</sub> P
Formula mass	580.98	610.97	567.96	675.54
System	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	C 2/c	C 2/c	P-1
a (Å)	10.9839(4)	20.3521(9)	21.6070(7)	10.5750(6)
b (Å)	12.3595(5)	20.4978(9)	12.1524(4)	12.4521(7)
c (Å)	12.5141(5)	15.1917(7)	19.2083(6)	13.0589(8)
α (°)	115.690(2)	90	90	69.599(3)
β (°)	108.072(2)	104.876(2)	102.879(2)	68.263(3)
γ (°)	100.254(2)	90	90	71.979(3)
$V(\text{\AA}^3)$	1355.13(10)	6125.2(5)	4916.9(3)	1464.70(15)
Ζ	2	8	8	2
T (K)	100(2)	100(2)	100(2)	100(2)
$\mu$ (mm <sup>-1</sup> )	1.043	0.930	1.147	0.959
D <sub>calc</sub> (Mg/m <sup>3</sup> )	1.424	1.325	1.534	1.532
θ max (°)	26.999	25.999	30.050	27.000
Data collected	26771	79236	153829	51180
Unique refl. / R <sub>int</sub>	5889 / 0.0770	6021 / 0.0346	7171 / 0.0230	6401 / 0.0414
Parameters / Restraints	526 / 269	368 / 18	379 /42	375 / 0
Goodness-of-Fit on F <sup>2</sup>	1.136	1.073	1.057	1.036
R1 / wR2 (all data)	0.0544 / 0.1509	0.0515 / 0.1386	0.0308 / 0.0741	0.0373 / 0.0875

### Table S1. Crystallographic data and processing parameters

1-ClO <sub>4</sub>			
Cu1-N2A	2.11(2)	Cu1-N6	2.231(3)
Cu1-N1	2.098(3)	Cu1-Cl1	2.2762(10)
Cu1-N4A	2.146(17)		
N2A-Cu1-N4A	163.0(9)	N1-Cu1-Cl1	147.71(11)
2-ClO <sub>4</sub>			
Cu1-N4	1.997(3)	Cu1-N2	1.995(3)
Cu1-N6	2.246(3)	Cu1-Cl1	2.3023(11)
Cu1-N1	2.134(2)		
N2-Cu1-N4	166.34(12)	N1-Cu1-Cl1	153.33(8)
4-ClO <sub>4</sub>			
Cu1-N1	2.2248(13)	Cu1-N7	2.053(15)
Cu1-N3	2.0199(13)	Cu1-N9	2.213(12)
Cu1-N5	1.9880(12)	Cu1-Cl1	2.2727(5)
N3-Cu1-N5	165.67(5)	N1-Cu1-Cl1	142.10(4)
5-PF <sub>6</sub>			
Cu1-N5	2.0027(18)	Cu1-N1	2.1710(18)
Cu1-N7	2.0164(18)	Cu1-Cl1	2.2810(6)
Cu1-N3	2.1551(19)		
N5-Cu1-N7	165.72(7)	N1-Cu1-Cl1	148.25(5)
6 [Cu(bedmpzp)Cl]PF <sub>6</sub> <sup>a)</sup>			
Cu1-N1	2.005(4)	Cu1-N3	1.991(4)
Cu1-N2	2.147(4)	Cl1-N1	2.2868(12)
Cu1-N5	2.291(4)		
N2-Cu1-Cl1	161.64(11)	N3-Cu1-N1	166.17(15)

Table S2. Selected bond distances (Å) and bond angles (°) of complexes  $1-CIO_4$ ,  $2-CIO_4$ ,  $4-CIO_4$  and  $5-PF_6$ .

<sup>a)</sup> Data taken from Ref 38

# **Table S3**. Non-covalent interactions of **1-CIO**45-Membered Ring (1) N3A-->C12AC12A-->C12A

5-Men	nbered	Ring (1)	N3A>	> N4A	·> C1	2A>	C11A	-> C10A	١		
5-Men	nhered	Ring $(2)$	N3B>	> N4R	> C1	19>	C10 -	-> C17	2		
6-Men	nhered	Ring $(4)$	N2A>	> C2A	> C3	βΔ>	C4A	-> C5A	, >	C6A	
6-Men	nbered	Ring $(5)$	N2B>	> C2B	> C3	3B>	C4B	> C5B	>	C6B	
Ding Int	torootio	no with C		tanaaa	< 60 00	a Alph	o < 20 000		oto <		
Ring-ini	leraciio		g-Cg Disi	lances	< 0.0 An	g., Aiph	a < 20.000	л Deg., Б	ela <	60.0 Deg.	
- Cg(I) - Alpha	= Plai = Dih	ne numbe nedral Anc	r I (= ring ile betwe	i numbe en Plar	er in () abo nes Land .	ove) J (Dea)					
- Beta	= And	ale Ca(I)	>Ca(J) o	r Ca(I)	->Me vect	tor and r	normal to p	lane I (De	ea)		
- Gamm	na = À	Angle Cg(	I)>Cq(J	) vector	and norn	nal to pla	ane J (Deq	ı) `	0/		
- Cg-Cg	a = Di	stance be	tween rin	ng Cent	roids (Ang	а.)		,			
- Cgl_P	erp = F	Perpendicu	ular dista	nce of (	Cg(I) on ri	ng J (Ar	ıg.)				
- CgJ_F	Perp = F	Perpendic	ular dista	ince of	Cg(J) on	ring I (Ai	ng.)				
- Slippa	ige = D	istance be	etween C	g(I) and	Perpend	licular P	rojection o	f Cg(J) or	n Ring	I (Ang).	
Cg(I)	Cg(J)	[ARU(J	J)] Cg-	Cg	Alpha	Beta	Gamma	Cgl_Pe	erp	CgJ_Perp	Slippage
Cg1	Cg1	[2667.0	01] 4.98	80(8)	0	49.8	49.8	3.214(7	7)	3.214(7)	3.805
Cg1	Cg2	[1555.0	01] 4.96	67(6)	88.0(7)	57.0	50.5	3.160(5	5)	2.707(2)	
Cg1	Cg3	[2666.0	01] 4.80	09(15)	12	37.1	38.0	3.790(7	7)	3.835(14)	2.901
Cg1	Cg4	[2666.0	01]   4.5	77(9)	20.5(9)	33.4	28.2	4.035(6	5)	3.821(7)	
Cg1	Cg5	[2667.0	01] 5.20	62(10)	12	50.9	41.8	3.922(6	5)	3.317(9)	4.085
Cg2	Cg1	[1555.0	01]   4.96	67(6)	88.0(7)	50.5	57.0	2.707(2	2)	3.160(5)	
Cg2	Cg1	[2667.0	01]   4.93	32(5)	88.0(7)	10.9	84.1	0.508(2	2)	4.843(5)	
Cg2	Cg2	[2556.0	01]   4.62	20(3)	0.0(2)	41.5	41.5	3.4577	(14)	3.4577(14)	3.064
Cg2	Cg3	[1555.0	01]   5.02	29(12)	80	50.9	59.4	2.563(2	2)	3.170(11)	
Cg2	Cg4	[1555.0	01] 5.3	57(6)	73.6(6)	50.8	62.9	2.445(2	2)	3.383(5)	
Cg2	Cg5	[1555.0	01] 5.30	04(9)	77.8(8)	51.6	62.2	2.477(2	2)	3.291(7)	
Cg2	Cg5	[2667.0	01] 4.89	90(7)	77.8(8)	15.5	71.4	1.562(2	2)	4.712(7)	
Cg3	Cg1	[2666.0	01] 4.80	09(15)	12	38.0	37.1	3.835(1	14)	3.790(7)	2.961
Cg3	Cg2	[1555.0	01] 5.02	28(12)	80	59.4	50.9	3.170(1	11)	2.563(2)	
Cg3	Cg5	[2666.0	01] 4.5 <sup>·</sup>	17(16)	23	36.0	28.9	3.953(1	14)	3.655(9)	
Cg4	Cg1	[2666.0	01] 4.5	76(9)	20.5(9)	28.2	33.4	3.821(7	7)	4.034(6)	
Cg4	Cg3	[2555.0	01] 5.68	85(12)	10	58.0	60.4	2.806(7	7)	3.015(14)	4.820
Cg4	Cg4	[2555.0	01] 5.38	86(8)	0.0(9)	55.9	55.9	3.021(7	7)	3.021(7)	4.459
Cg4	Cg5	[2666.0	01] 4.29	95(11)	29	26.6	26.1	3.857(7	7)	3.840(9)	
Cg5	Cg1	[2667.0	01] 5.26	62(10)	12	41.8	50.9	3.317(9	9)	3.922(6)	3.508
Cg5	Cg3	[2666.0	01] 4.5	17(16)	23	28.9	36.0	3.656(9	9)	3.953(14)	
Cg5	Cg4	[2666.0	01] 4.29	95(11)	29	26.1	26.6	3.840(9	9)	3.857(7)	
Cg5	Cg5	[2667.0	01]   5.5	58(12)	0	43.4	43.4	4.039(9	9)	4.039(9)	3.817
[ 2667]	= 1-X,	1-Y,2-Z									
[ 1555]	= X, Y,										
	= 1 - X, 1	1-Y,1-Z									
[ 2555]	= -X,-1   =	(, I-Z									
[ 2000]	,,-	,-2									
Analysis	s of X-ł	HCg(Pi-I	Ring) Inte	eraction	s (HCg ·	< 3.0 An	g Gamm	a < 40.0	Deg)		
- Cq(J)	= Cer	iter of grav	vity of rin	q J (Pla	ine numb	er above	e)				
- H-Per	p = Pe	rpendicula	ar distanc	e of H	to ring pla	ine J	,				
- Gamm	na = A	ingle betw	een Cg-ł	H vecto	r and ring	J norma	al				
- X-HC - XCg	Cg = X-l = Dist	H-Cg angl ance of X	e (degre to Cg (A	es) .ngstror	n)						
ХЦ/I	)   [			<u>م</u> ا		НСа		rn C	ammo		XCa
C11A	, <u> </u>	H11A		A]	667 011	2 QU	2 9 7	<u>ס</u> קו	74	155	3 787(10)
C20				[2	556 011	2.50	2.07	<u>0</u> . ว	15	142	3.535(4)
C13P		H13F	Ca5	[2]	666 011	2.93	2 30	3. ຊຸ	3 43	144	3 774(16)
0.00			- 595	1 [2]		2.00	2.00	1.00		177	0.114(10)
[ 2667]	= 1-X,   = -X -)	1-Y,2-Z ( 1-7									

[2666] = 1-X, 1-Y, 1-Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in () in the Ring-Analysis above

Cg(I)	X	у	z	Хо	Yo	Zo
Cg1	0.5951(5)	0.5379(5)	0.8574(5)	2.024(6)	1.213(7)	8.698(5)
Cg2	0.12824(16)	0.21432(16)	0.66024(13)	-1.6260(19)	-1.497(2)	6.6976(14)
Cg3	0.1297(10)	0.2385(10)	0.2697(10)	-0.147(12)	1.224(14)	2.736(10)
Cg4	0.1427(6)	0.2187(5)	0.2381(5)	0.162(6)	1.180(7)	2.415(5)
Ca5	0.6322(7)	0.5448(7)	0.8583(7)	2,414(9)	1,291(9)	8,707(7)

Analysis of Potential Hydrogen Bonds and Schemes

Res	Donor	HAcceptor	[ARU]	D-H	HA	DA	D-HA
4>05	H90		?	0.91			
1>C8A	H8AB	01	[1555.02]	0.99	2.57	3.512(9)	158
1>C8A	H8AB	03	[1555.02]	0.99	2.41	2.936(8)	112'
1>C4A	H4A	02	[1454.02]	0.95	2.53	3.267(9)	135
1>C7A	H7A3	Cl1	[]	0.98	2.63	3.42(2)	137
1>C5A	H5A	04	[1454.02]	0.95	2.51	3.363(17)	149
1>C1A	H1AA	Cl1	[2666.01]	0.99	2.73	3.711(8)	174
1>C9A	H9AB	Cl1	[2666.01]	0.99	2.80	3.593(8)	138
1>C14A	H14A	Cl1	[]	0.98	2.60	3.415(17)	141
C18	H18	03	[1455.02]	0.95	2.38	3.263(7)	155

:: No Classic Hydrogen Bonds Found

Translation of ARU-Code to CIF and Equivalent Position Code

[ 2666.] = [ 2\_666] = 1-x,1-y,1-z [ 1454.] = [ 1\_454] = -1+x,y,-1+z [ 1455.] = [ 1\_455] = -1+x,y,z

### Table S4. Non-covalent interactions of 2-CIO<sub>4</sub>

5-Membere 6-Membere 6-Membere	ed Ring (2) ed Ring (3) ed Ring (4) ed Ring (6)	N3 N5 Cu1 - N2	-> N4 -> N6 > N1 -> C2	> ( > ( >	C13 C20 C9 C3 -	> C12 > C12 > C19 > C10 -> C4	2> C 9> C 9> N > C5	- 11 18 3>	N4 C6			
Ring-Interact	tions with C	g-Cg Dis	stances <	< 6.0	Ang., A	Alpha <	20.000 D	eg., Bet	a < 60.	0 Deg.		
- Cg(I) = P - Alpha = E - Beta = A - Gamma = - Cg-Cg = - CgL_Perp = - CgJ_Perp = - Slippage =	lane numbe Dihedral Ang ngle Cg(I) = Angle Cg(I Distance be = Perpendicu = Perpendicu Distance be	r I (= ring le betwe >Cg(J) c )>Cg( )>Cg( tween ri lar dista ular dista tween C	g numbe een Plan or Cg(I) I) vector ng Centr ance of C ance of C Cg(I) and	r in () ; es I ar >Me v and no roids ( <i>I</i> Cg(I) or Cg(J) o Perpe	above) nd J (D ector a ormal t Ang.) n ring J on ring endicula	eg) nd norm o plane I (Ang.) I (Ang.) ar Projec	al to plar J (Deg) ction of C	ne I (Deg g(J) on I	I) Ring I ( <i>i</i>	Ang).		
Cg(I) Cg	(J) [ARU	(J)] C	g-Cg	Alpha	a	Beta	Gamma	Cgl F	Perp	CgJ Pe	rp	Slippage
Cq2 Cq	6 [7667	.01] 4	.576(2)	23.12	2(19)	13.2	26.1	4.109	2(15)	4.4553(	14)	
Ca3 Ca	3 [7666	.011 4	.519(2)	0.0(2	)	43.7	43.7	3.267	7(17)	3.2677(	17)	3.122
Ca3 Ca	6 [1555	.011 4	.868(2)	84.60	(2)	35.1	51.9	3.003	4(16)	3.9813(	15)	_
Ca6 Ca	2 [7667	.011 4	.576(2)	23.12	2(19)	26.1	13.2	4.455	2(14)	4.1092(	15)	
Ca6 Ca	3 [1555	.011 4	.868(2)	84.60	(2)	51.9	35.1	3.981	2(15)	3.0034(	16)	
Ca6 Ca	6 [2656	.011 4	.343(2)	6.16	(17)	39.3	39.3	3.361	1(14)	3.3610(	14)	2.750
<ul> <li>Analysis of X-HCg(Pi-Ring) Interactions (HCg &lt; 3.0 Ang Gamma &lt; 40.0 Deg)</li> <li>- Cg(J) = Center of gravity of ring J (Plane number above)</li> <li>- H-Perp = Perpendicular distance of H to ring plane J</li> <li>- Gamma = Angle between Cg-H vector and ring J normal</li> <li>- X-HCg = X-H-Cg angle (degrees)</li> <li>- XCg = Distance of X to Cg (Angstrom)</li> </ul>												
- X-HCg = X - XCg = D	K-H-Cg angl istance of X	een Cg- e (degre to Cg (A	H vector es) Angstron	and ri	ing J n	J ormal						
- X-HCg = X - XCg = D	K-H-Cg angl istance of X	een Cg- e (degre to Cg (A	H vector es) Angstron	and ri	ing J no	J ormal Cq	H-Perp	Gar	nma	X-HCo	3	XCq
- Gamma = - X-HCg = X - XCg = D	K-H-Cg angl istance of X H(I) -H8C	een Cg- e (degre to Cg (A Cg(J) Ca3	H vector ees) Angstron	n) RU(J)]	ing J no	J ormal Cg 3	H-Perp -2.58	Gar 24.3	nma	X-HCç 148	3	XCg 3.704(5)
- Gamma = - X-HCg = X - XCg = D X C8 C21	Highe betw K-H-Cg anglistance of X H(I) -H8C -H21C	een Cg- e (degre to Cg (/ Cg(J) Cg3 Cg3	H vector ees) Angstron [Al [26] [76]	RU(J)]	H 2.8 2.6	J ormal Cg 3 1	H-Perp -2.58 2.61	Gar 24.3 1.25	nma 37 5	X-HCç 148 139	]	XCg 3.704(5) 3.417(5)
$\begin{array}{r} - \text{ Gamma} = \\ - \text{ X-H.}\text{Cg} =  \\ - \text{ XCg} =  \\ \hline \text{ X} \\ \hline \text{ C8} \\ \hline \text{ C21} \\ \hline \\ \hline \begin{array}{r} 2656 \\ 1 = 1-2 \\ \hline \\ \hline \\ 7666 \\ 1 = 3/2 \\ \hline \\ $	Angle betw K-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin x 0.89122 0.71782 0.59747	een Cg- e (degre to Cg (/ Cg(J) Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(7)	H vector ees) Angstrom [Al [26 [76 [76 [76 [76 [76 [76 [76]] [76] [76	Ning and rin (N) (S56.01 (S66.01 (S66.01 (S66.01 (S66.01 (S66.01 (S66.01 (S66.01 (S66.01 (S66.01 (S66.01) (S66.01 (S66.01) (S	H   2.8   2.6   2.6   2.6   2.6   2.6   2.6   2.6   2.6   1.5 	J prmal Cg 3 1 given ir 354(10) 328(11) 063(10)	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15)	nma 37 5 alysis a Yo 13.60 16.43 16.03	X-HCc 148 139 above 57(17) 97(17) 62(14)	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14)
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F	Angle betw X-H-Cg anglistance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin x 0.89122 0.71782 0.59747 Potential Hyd	een Cg- e (degre to Cg ( <i>I</i> Cg(J) Cg3 Cg3 Z ng Centr 2(8) 2(8) 7(7) drogen E	H vector ees) Angstrom [Al [26 [26 [76 [76 [76 [76 [76 [76 [76]] [26 [76]] [26] [76] [26] [26] [26] [26] [26] [26] [26] [2	× and ri n) RU(J)] 556.01 566.01 566.01 566.01 (8) (8) (8) (7) 10 10 10 10 10 10 10 10 10 10	H H 2.8 2.6 1 2.6 1 2.6 0.853 0.613 0.855 0.855 emes	J prmal Cg 3 1 given ir 354(10) 328(11) 063(10)	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15)	nma 37 5 alysis a 13.60 16.43 16.03	X-HCc 148 139 above 57(17) 97(17) 62(14)	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14)
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = 3/ $\lambda$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res	Angle betw K-H-Cg anglistance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin X 0.89122 0.71782 0.59747 Potential Hyd	een Cg- e (degre to Cg ( <i>I</i> Cg(J) Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 4(7) drogen E	H vector ees) Angstrom [A] [26 [76 [76 [76 [76 [76 [76 [76 [76] [76]	RU(J)]       S56.01       S56.01       S66.01       S67.01 <td< td=""><td>H         H         2.8         Model         2.8         0.853         0.613         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853</td><td>J prmal Cg 3 1 given ir 354(10) 328(11) 063(10)</td><td>H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423</td><td>Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA</td><td>nma 37 5 alysis a 13.60 16.43 16.03</td><td>X-HCc 148 139 above 57(17) 97(17) 62(14)</td><td>Zo 12. 9.0 12.</td><td>XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA</td></td<>	H         H         2.8         Model         2.8         0.853         0.613         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853         0.853	J prmal Cg 3 1 given ir 354(10) 328(11) 063(10)	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA	nma 37 5 alysis a 13.60 16.43 16.03	X-HCc 148 139 above 57(17) 97(17) 62(14)	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5	Angle betw X-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin X 0.89122 0.71782 0.59747 Potential Hyd Donor H1A	een Cg- e (degre to Cg ( <i>I</i> Cg(J) Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(7) drogen E H	H vector ees) Angstrom [Al [26 [76 [76 [76 [76 [76 [76 [76 [76]] [76] [76	<ul> <li>and ri</li> <li>and ri</li> <li>RU(J)]</li> <li>356.01</li> <li>356.01</li> <li>366.01</li> <li>wity nu</li> <li>(8)</li> <li>(7)</li> <li>(8)</li> <li>(7)</li> <li>(7)</li> <li>(8)</li> <li>(7)</li> <li>(7)&lt;</li></ul>	H           2.8           2.8           2.8           2.8           2.8           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853           0.853	J prmal Cg 3 1 given ir 354(10) 328(11) 963(10) D-H 0.95	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15) HA 2.69 2.41	nma 37 5 alysis a 13.60 16.43 16.03	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 0A 0A	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6	Angle betw X-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1 fer to the Rin x 0.89122 0.71782 0.59747 Potential Hyd H1A H5 H/C	een Cg- e (degre to Cg (/ Cg3 Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(7) drogen E H 	H vector ees) Angstrom [Al [26 [76 [76 [76 [76 [76 [76] [76] [76] [76	<ul> <li>and rig</li> <li>and rig</li> <li>RU(J)]</li> <li>356.01</li> <li>356.01</li> <li>366.01</li> <li>366.01<td>H         2.8         2.8         2.8         2.8         2.8         0.853         0.613         0.854         0.855         0.853         0.854         0.855         0.855         0.856         0.856         0.856</td><td>J prmal Cg 3 1 given ir 354(10) 328(11) 963(10) 063(10) 0.96 0.96</td><td>H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423</td><td>Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15) HA 2.69 2.41 2.50</td><td>nma 37 5 alysis a 13.60 16.43 16.03</td><td>X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 0A 0A 0A 0A 0A</td><td>Zo 12. 9.0 12.</td><td>XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157</td></li></ul>	H         2.8         2.8         2.8         2.8         2.8         0.853         0.613         0.854         0.855         0.853         0.854         0.855         0.855         0.856         0.856         0.856	J prmal Cg 3 1 given ir 354(10) 328(11) 963(10) 063(10) 0.96 0.96	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15) HA 2.69 2.41 2.50	nma 37 5 alysis a 13.60 16.43 16.03	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 0A 0A 0A 0A 0A	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C6 C6 C6	Angle betw X-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin x 0.89122 0.71782 0.59747 Potential Hyd Potential Hyd H1A H5 H6	een Cg- e (degre to Cg (/ Cg3 Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8)	H vector ees) Angstrom [Al [26 [26 [76 [76] [76] [76] [76] [76] [76] [76]	<ul> <li>and ri</li> <li>and ri</li> <li>RU(J)]</li> <li>356.01</li> <li>356.01</li> <li>366.01</li> <li>366.01</li></ul>	H           H           2.8           2.8           2.8           2.8           0.853 </td <td>J prmal Cg 3 1 given ir 354(10) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(10)</td> <td>H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423</td> <td>Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51</td> <td>nma 37 5 alysis a 13.60 16.43 16.03 16.03</td> <td>X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5)</td> <td>Zo 12. 9.0 12.</td> <td>XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134</td>	J prmal Cg 3 1 given ir 354(10) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(11) 328(10)	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51	nma 37 5 alysis a 13.60 16.43 16.03 16.03	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5)	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C10 C10 C11	Angle betw Angle betw K-H-Cg anglistance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1 fer to the Rin x 0.89122 0.71782 0.59747 Potential Hyd H1A H5 H10B	een Cg- e (degre to Cg (/ Cg3 Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8)	H vector ees) Angstrom [Al [26 [76 [76 [76] [76] [76] [76] [76] [76]	<ul> <li>and ri</li> <li>and ri</li> <li>RU(J)]</li> <li>356.01</li> <li>356.01</li></ul>	Image       H         Image       Image         Ima	J prmal Cg 3 1 given ir 354(10) 328(11)	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.59 2.51	nma 37 5 alysis a 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5) 3.227(9)	Zo 12. 9.0 12.	XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 132
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C10 C14 C14 C14	Angle betw Angle betw K-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin x 0.89122 0.71782 0.59747 Potential Hyd Potential Hyd H1A H6 H10B H14A	een Cg- e (degre to Cg ( <i>I</i> ) Cg3 Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8)	H vector ees) Angstrom [Al [26 [76 [76 [76 [76 [76 [76] [76] [76] [76	<ul> <li>and rig</li> <li>and rig</li> <li>RU(J)]</li> <li>356.01</li> <li>356.01</li> <li>366.01</li> <li>366.01<td>H           H           2.8           2.8           2.8           2.8           0.853           0.613           0.850           emes           RU]           56.02]           55.02]           55.02]</td><td>J prmal Cg 3 1 given ir 054(10) 028(11) 063(10) 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98</td><td>H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423</td><td>Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.51 2.44</td><td>nma 37 5 alysis a 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3</td><td>X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 6.453(4) 3.309(9) 3.322(5) 3.322(5) 3.329(6) 102(42)</td><td></td><td>XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 132 153</td></li></ul>	H           H           2.8           2.8           2.8           2.8           0.853           0.613           0.850           emes           RU]           56.02]           55.02]           55.02]	J prmal Cg 3 1 given ir 054(10) 028(11) 063(10) 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 94(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.51 2.44	nma 37 5 alysis a 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 6.453(4) 3.309(9) 3.322(5) 3.322(5) 3.329(6) 102(42)		XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 132 153
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C10 C14 C14 C14 C14	Angle betw Angle betw K-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin X 0.89122 0.71782 0.59747 Potential Hyd H1A H1A H10B H14B H14B	een Cg- e (degre to Cg ( <i>J</i> ) Cg3 Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(7) drogen E 07 05 06 05	H vector ees) Angstrom [Al [26 [26 [276 [276 [276 [276 [276]	<ul> <li>and rig</li> <li>and rig</li> <li>RU(J)]</li> <li>356.01</li> <li>356.01</li> <li>366.01</li> <li>366.01<td>Image       H         Image       H         Image       2.8         Imbers       2.8         Imbers       0.853         0.613       0.850         0.853       0.613         0.850       0.850         0.613       0.850         0.650       0.613         0.650       0.650         0.650.02]       0.550.02         0.650.02       0.550.02         0.650.02       0.550.02         0.650.02       0.550.02</td><td>J prmal Cg 3 1 given ir 254(10) 228(11) 263(10) 263(10) 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98</td><td>H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423</td><td>Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.44 2.22 2.62</td><td>nma 37 5 alysis a 13.60 16.43 16.03 16.03 16.3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3</td><td>X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5) 3.322(5) 3.3257(9) 3.339(6) 3.163(10)</td><td></td><td>XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 132 153 160 455</td></li></ul>	Image       H         Image       H         Image       2.8         Imbers       2.8         Imbers       0.853         0.613       0.850         0.853       0.613         0.850       0.850         0.613       0.850         0.650       0.613         0.650       0.650         0.650.02]       0.550.02         0.650.02       0.550.02         0.650.02       0.550.02         0.650.02       0.550.02	J prmal Cg 3 1 given ir 254(10) 228(11) 263(10) 263(10) 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.44 2.22 2.62	nma 37 5 alysis a 13.60 16.43 16.03 16.03 16.3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5) 3.322(5) 3.3257(9) 3.339(6) 3.163(10)		XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 132 153 160 455
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C10 C14 C14 C14 C14 C14 C14	Angle betw Angle betw K-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin X 0.89122 0.71782 0.59747 Potential Hyd Donor H1A H5 H6 H10B H14A H14B H14C	een Cg- e (degre to Cg ( <i>J</i> ) Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8)	H vector ees) Angstrom [Al [26 [26 [276 [26] [276 [26] [276 [26] [276 [26] [276 [26] [276 [26] [276] [	r [AF [45 [45 [45 [45 [45 [45 [45 [45	Image       H         Image       H         Image       2.8         Imbers       0.853         0.613       0.853         0.613       0.850         0.850       0.850         emes       0.850         RUJ       56.02]         55.02]       55.02]         55.02]       55.02]         55.02]       55.02]	J prmal Cg 3 1 given ir 354(10) 228(11) 263(10) 263(10) 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98 0.98	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.44 2.22 2.30 2.51	nma 37 5 alysis a Yo 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3 3 3	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5) 3.322(5) 3.3257(9) 3.339(6) 3.183(10) 5.187(12) 5.187(12)		XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 157 134 153 160 150 150
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C10 C14 C14 C14 C14 C15 C42 C15 C6 C15 C15 C15 C15 C15 C15 C15 C15	Angle betw Angle betw K-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin X 0.89122 0.71782 0.59747 Potential Hyd Donor H1A H5 H6 H10B H14A H14B H14C H15C	een Cg- e (degre to Cg ( <i>J</i> ) Cg3 Cg3 Z ng Centr 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8) 2(8)	H vector ees) Angstrom [Al [26 [26 [276 [26 [276 [26 [276 [26 [276] [276] [26 [26 [276] [2	r [AF [66] [7] [7] [7] [66] [7] [66] [66] [66	Image       H         Image       H         Image       2.8         Imbers       1         Imbers       0.853         0.613       0.850         0.850 <td>J prmal Cg 3 1 given ir 354(10) 228(11) 263(10) 228(11) 263(10) 0.98 00000000000000000000000000000000000</td> <td>H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423</td> <td>Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.44 2.22 2.30 2.79 2.70 2.70</td> <td>nma 37 5 alysis a Yo 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3 3 3</td> <td>X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5) 3.322(5) 3.322(5) 3.339(6) 3.163(10) 3.187(12) 3.512(4)</td> <td></td> <td>XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 157 134 153 160 150 131 495</td>	J prmal Cg 3 1 given ir 354(10) 228(11) 263(10) 228(11) 263(10) 0.98 00000000000000000000000000000000000	H-Perp -2.58 2.61 () in the Xo 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.44 2.22 2.30 2.79 2.70 2.70	nma 37 5 alysis a Yo 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3 3 3	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.453(4) 3.309(9) 3.322(5) 3.322(5) 3.322(5) 3.339(6) 3.163(10) 3.187(12) 3.512(4)		XCg 3.704(5) 3.417(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 157 134 153 160 150 131 495
- Gamma = - X-HCg = $\lambda$ - XCg = D X C8 C21 [ 2656] = 1- $\lambda$ [ 7666] = $3/2$ The Cg(I) ref Cg(I) Cg2 Cg3 Cg6 Analysis of F Res C1 C5 C6 C10 C14 C14 C14 C14 C15 C16 C17	Angle betw K-H-Cg angli istance of X H(I) -H8C -H21C X,Y,3/2-Z 2-X,3/2-Y,1- fer to the Rin X 0.89122 0.71782 0.59747 Potential Hyd Donor H1A H5 H6 H10B H14B H14B H14C H15C H16A	een Cg- e (degre to Cg (/ Cg(J) Cg3 Cg3 Z ng Centr 2(8) 2(8) 7(7) drogen E (8) 7(7) drogen E (1,07 05 06 07 07 07 07	H vector ees) Angstrom [Al [26 [26 [276 [26 [276 [26 [276 [26 [26 [276 [26 [26 [26 [26 [26 [26 [26 [26 [26 [2	<ul> <li>N (J)</li> <li>RU(J)]</li> <li>S56.01</li> <li>S56.01</li> <li>S66.01</li> <li>S66.0</li></ul>	Image       H         Image       H         Image       2.8         Imbers       1         Imbers       0.853         0.613       0.613         0.853       0.613         0.853       0.613         0.6502       1         556.02       1         556.02       1         556.01       1         556.01       1	J prmal Cg 3 1 given ir 354(10) 3554(10) 3554(10	H-Perp -2.58 2.61 2.61 14.809 12.217 8.8423	Gar 24.3 1.25 Ring-An 24(17) 72(17) 3(15) HA 2.69 2.41 2.59 2.51 2.44 2.22 2.30 2.79 2.59 2.59 2.59	nma 37 5 alysis a Yo 13.60 16.43 16.03 16.03 3 3 3 3 3 3 3 3 3 3 3 3 3	X-HCc 148 139 above 57(17) 97(17) 62(14) 0A 3.309(9) 3.322(5) 3.227(9) 3.329(6) 3.339(6) 3.339(6) 3.339(6) 3.339(6) 3.329(6) 3.339(6) 3.339(6) 3.322(5) 3.327(5) 3.377(5)		XCg 3.704(5) 3.417(5) 5321(15) 045(16) 4895(14) D-HA 134 157 134 157 134 153 160 150 131 136 160

C19	H19	06A	[7666.02]	0.95	2.56	3.456(11)	156
C19	H19	O6B	[7666.02]	0.95	2.55	3.498(9)	172'
C21	H21A	04	[7666.02]	0.98	2.55	3.474(5)	157
C22	H22B	Cl1	0	0.98	2.72	3.652(4)	159
C22	H22C	05	[6656.02]	0.98	2.48	3.372(6)	151
:: No Classio	c Hydrogen Bo	onds Found					

Translation of ARU-Code to CIF and Equivalent Position Code

[7667.] = [7\_667] = 3/2-x,3/2-y,2-z [2656.] = [2\_656] = 1-x,y,3/2-z [6656.] = [4\_656] = 3/2-x,1/2+y,3/2-z [4565.] = [6\_566] = x,1-y,1/2+z [2756.] = [2\_756] = 2-x,y,3/2-z [7666.] = [7\_666] = 3/2-x,3/2-y,1-z

#### Table S5. Non-covalent interactions of 4-CIO<sub>4</sub>

5-Membered Ring (1)	N2	>	N3	>	C4	>	C3	>	C2
5-Membered Ring (2)	N4	>	N5	>	C11	>	C10	>	C9
5-Membered Ring (3)	N8	>	N9	>	C1C	>	C1B	>	C1A
5-Membered Ring (4)	N6	>	N7	>	C18	>	C17	>	C16

Ring-Interactions with Cg-Cg Distances <6.0 Ang., Alpha <20.0 Deg., Beta <60.0 Deg.

- Cg(I) = Plane number I (= ring number in () above)

- Alpha = Dihedral Angle between Planes I and J (Deg)

- Beta = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)

- Gamma = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)

- Cg-Cg = Distance between ring Centroids (Ang.)

- Cgl\_Perp = Perpendicular distance of Cg(I) on ring J (Ang.)

- CgJ\_Perp = Perpendicular distance of Cg(J) on ring I (Ang.)

- Slippage = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).

						-			
Cg(I)	Cg(J)	[ARU(J)]	Cg-Cg	Alpha	Beta	Gamma	Cgl_Perp	CgJ_Perp	Slippage
Cg1	Cg1	[7636.01]	5.6364(9)	0.00(9)	44.4	44.4	4.0252(7)	4.0251(7)	3.946
Cg1	Cg2	[7636.01]	5.5172(10)	44.99(10)	24.5	56.4	3.0551(7)	5.0185(7)	
Cg1	Cg3	[1555.01]	4.525(5)	73.8(5)	29.1	44.7	3.2185(6)	3.953(5)	
Cg1	Cg3	[2756.01]	5.596(5)	76.0(5)	26.0	82.8	0.7006(6)	5.029(5)	
Cg1	Cg4	[1555.01]	4.366(5)	66.6(5)	31.1	36.2	3.5227(6)	3.737(5)	
Cg1	Cg4	[2756.01]	5.473(6)	76.5(5)	28.3	85.2	0.4586(6)	4.819(5)	
Cg2	Cg1	[7636.01]	5.5171(10)	44.99(10)	56.4	24.5	5.0186(7)	3.0550(7)	
Cg2	Cg3	[6646.01]	5.547(5)	85.2(5)	12.3	74.2	1.5062(7)	5.419(5)	
Cg2	Cg4	[6646.01]	5.919(5)	79.9(5)	11.9	69.1	2.1090(7)	5.792(5)	
Cg3	Cg1	[1555.01]	4.526(5)	73.8(5)	44.7	29.1	3.953(5)	3.2186(6)	
Cg3	Cg2	[1555.01]	4.994(5)	89.0(5)	57.4	68.9	1.796(5)	2.6912(7)	
Cg3	Cg3	[2756.01]	4.602(8)	3.9(7)	34.6	34.6	3.788(5)	3.787(5)	2.615
Cg3	Cg4	[2756.01]	4.609(8)	11.2(7)	34.7	41.0	3.477(5)	3.789(5)	2.624
Cg4	Cg1	[1555.01]	4.366(5)	66.6(5)	36.2	31.1	3.737(5)	3.5228(6)	
Cg4	Cg3	[2756.01]	4.608(8)	11.2(7)	41.0	34.7	3.789(5)	3.476(5)	3.025
Cg4	Cg4	[2756.01]	4.583(8)	16.9(8)	39.8	39.8	3.522(5)	3.522(5)	2.933

[ 7636] = 3/2-X,-3/2-Y,1-Z

[ 1555] = X,Y,Z

[ 2756] = 2-X,Y,3/2-Z

[ 6646] = 3/2-X,-1/2+Y,3/2-Z

Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 40.0 Deg)

- Cg(J) = Center of gravity of ring J (Plane number above)

- H-Perp = Perpendicular distance of H to ring plane J

- Gamma = Angle between Cg-H vector and ring J normal

- X-H..Cg = X-H-Cg angle (degrees)

- X..Cg = Distance of X to Cg (Angstrom)

Х	H(I)	Cg(J)	[ARU(J)]	HCg	H-Perp	Gamma	X-HCg	XCg
C1D	-H1DC	Cg2	[6656.01]	2.78	-2.67	16.13	130	3.485(9)
C8	-H8B	Cg1	[7636.01]	2.89	-2.81	13.30	145	3.7393(16)

[ 6656] = 3/2-X,1/2+Y,3/2-Z

[ 7636] = 3/2-X,-3/2-Y,1-Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in () in the Ring-Analysis above

Cg(I)	Х	у	Z	Хо	Yo	Zo
Cg1	0.87880(3)	-0.69603(6)	0.55256(3)	16.6230(7)	-8.4584(7)	10.3468(6)
Cg2	0.66406(3)	-0.59649(6)	0.70930(4)	11.3120(7)	-7.2487(7)	13.2817(7)
Cg3	0.8986(2)	-0.5359(4)	0.7691(3)	16.123(5)	-6.513(5)	14.402(5)
Cg4	0.8989(3)	-0.5674(4)	0.7687(3)	16.132(6)	-6.896(5)	14.394(5)

Analysis of Potential Hydrogen Bonds and Schemes

Res	Donor	HAcceptor	[ARU]	D-H	HA	DA	D-HA
C3	H3	03	[2756.02]	0.95	2.60	3.547(2)	176
1>C1D	H1DB	02	[3747.02]	0.98	2.37	3.326(7)	165
C5	H5B	02	[2756.02]	0.98	2.59	3.517(2)	158
C5	H5C	02	[4544.02]	0.98	2.58	3.512(2)	159
C6	H6A	Cl1	0	0.98	2.71	3.5781(18)	148
C8	H8A	03	[6656.02]	0.99	2.58	3.307(2)	130
C14	H14B	N2		0.99	2.56	2.954(2)	104

:: No Classic Hydrogen Bonds Found

Translation of ARU-Code to CIF and Equivalent Position Code

[ 3747.] = [ 5\_747] = 2-x,-1-y,2-z [ 6656.] = [ 4\_656] = 3/2-x,1/2+y,3/2-z [ 4544.] = [ 6\_545] = x,-1-y,-1/2+z [ 2756.] = [ 2\_756] = 2-x,y,3/2-z

#### Table S6. Non-covalent interactions of 5-PF<sub>6</sub>

$            5-Membered Ring (1) Cu1 \rightarrow N1 \rightarrow C15 \rightarrow N6 \rightarrow N7            5-Membered Ring (2) N2 \rightarrow N3 \rightarrow C5 \rightarrow C4 \rightarrow C3            5-Membered Ring (3) N4 \rightarrow N5 \rightarrow C12 \rightarrow C11 \rightarrow C10            5-Membered Ring (5) Cu1 \rightarrow N1 \rightarrow C18 \rightarrow C17 \rightarrow C16            6-Membered Ring (6) Cu1 \rightarrow N1 \rightarrow C2 \rightarrow C2 \rightarrow N2            6-Membered Ring (6) Cu1 \rightarrow N1 \rightarrow C2 \rightarrow C2 \rightarrow N2            6-Membered Ring (7) C19 \rightarrow C20 \rightarrow C21 \rightarrow C22 \rightarrow N4 \rightarrow N5            6-Membered Ring (7) C19 \rightarrow C20 \rightarrow C21 \rightarrow C22 \rightarrow C23 \rightarrow C24Ring-Interactions with Cg-Cg Distances < 6.0 Ang., Alpha < 20.000 Deg. and Beta < 60.0 Deg.             - Cg(1) = Plane number (= ring number in () above)- Alpha = Dihedral Angle between Planes I and J (Deg)            Beta = Angle Cg(1) \rightarrow Cg(1) \rightarrow Cg(1) \rightarrow We vector and normal to plane I (Deg)- Gg.Cg = Distance between ring Centroids (Ang.)- Cg.Cg = Distance between ring Centroids (Ang.)- Cg.Qg = Distance between ring Centroids (Ang.)- Cg.Qg = Distance between ring Centroids (Ang.)- Cg.Qg = Joistance between CG (0) on ring J (Ang.)- Silpage = Distance between CG (0) and Perpendicular Projection of Cg(J) on Ring I (Ang).            - P,Q,R,S = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)$						•				
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	5-Mem 5-Mem 5-Mem 6-Mem 6-Mem 6-Mem	ibered F ibered F ibered F ibered F ibered F ibered F ibered F	Ring (1) Cu Ring (2) N2 Ring (3) N4 Ring (4) N6 Ring (5) Cu Ring (6) Cu Ring (7) C1	11      >       N1         2      >       N3         4      >       N5         6      >       N7         11      >       N1         11      >       N1         12      >       N1         13      >       N2         14      >       N2         15      >       N2         16      >       N2         17      >       N2	> C15 > C5 - > C12 > C18 > C1 > C8 > C21	> N6 -> C4 > C1 > C1 > C2 > C9 > C	6> N > C3 1> C 7> C 7> N2 > N4 22> (	7 10 16 > N5 C23> C24	4	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ring-Int	eraction	s with Cg-C	g Distances <	6.0 Ang., A	Alpha <	20.000 De	eg. and Beta <	< 60.0 Deg.	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	- Cg(I) - Alpha - Beta - Gamm - Cg-Cg - CgI_P - CgJ_F - Slippa - P,Q,R	= Plane = Dihe = Angle na = An = Dis erp = Pe Perp = Pe ge = Dis S = J-F	e number I ( edral Angle b e Cg(I)>Cg ngle Cg(I)> tance betwe erpendicular erpendicular tance betwe Plane Param	= ring number between Plane g(J) or Cg(I)	in () above) → I and J (D → Me vector a and normal t bids (Ang.) g(I) on ring Cg(J) on ring Perpendicul h. Coord. (Xe	and norn to plane J (Ang.) I (Ang.) ar Proje o, Yo, Z	nal to plan J (Deg) ction of Cູ o)	e I (Deg) g(J) on Ring I	(Ang).	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg(I)	Cg(J )	[ARU(J)]	Cg-Cg	Alpha	Bet a	Gamm a	Cgl_Perp	CgJ_Perp	Slippag e
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg2	Cg3	[1555.01 ]	4.8080(16	81.61(14 )	49.6	56.2	2.6745(10	3.1158(10 )	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg2	Cg3	[2666.01	4.8080(16	81.61(14	14.9	84.0	0.5372(10	4.9575(10	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg2	Cg4	[1555.01	4.9143(15	82.00(14	51.5	51.6	3.0498(10	3.0613(10	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cg3	Cg2	[1555.01	4.8079(16	81.61(14	56.2	49.6	3.1157(10	2.6744(10	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cg3	Cg3	[2666.01	4.7155(16	0.00(14)	47.1	47.1	3.2116(10	3.2117(10	3.453
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cg3	Cg4	[2656.01	4.6885(15	14.96(13	38.6	24.3	4.2747(10	3.6666(9)	2.922
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cg3	Cg7	[2656.01	4.5953(14	36.31(13	21.4	54.0	2.6996(10	4.2779(10	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg4	Cg2	[1555.01	4.9143(15	82.00(14	51.6	51.5	3.0613(10	3.0497(10	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg4	Cg3	[2656.01	4.6885(15	14.96(13	24.3	38.6	3.6666(9)	4.2747(10	1.926
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Cg7	Cg2	[1545.01	5.9825(15	66.05(13	8.4	62.9	2.7265(10	5.9190(10	
$\left \begin{array}{c c c c c c c c c c c c c c c c c c c$	Cg7	Cg3	[2656.01	4.5952(14	36.31(13	54.0	21.4	4.2778(10	2.6995(10	
	Cg7	Cg7	] [2655.01 ]	3.9188(16 )	0.00(12)	23.2	23.2	) 3.6030(10 )	) 3.6030(10 )	1.541

[ 1555] = X,Y,Z

[ 2666] = 1-X,1-Y,1-Z

[ 2656] = 1-X,-Y,1-Z [ 1545] = X,-1+Y,Z

[ 2655] = 1-X,-Y,-Z

Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma < 40.0 Deg)

- Cg(J) = Center of gravity of ring J (Plane number above)
- H-Perp = Perpendicular distance of H to ring plane J

- Gamma = Angle between Cg-H vector and ring J normal

- X-H..Cg = X-H-Cg angle (degrees)
- X..Cg = Distance of X to Cg (Angstrom)
- X-H, Pi = Angle of the X-H bond with the Pi-plane (i.e.' Perp. = 90 degr., Para. = 0 degr.)

X	H(I)	Cg(J)	[ARU(J)]	HCg	H-Perp	Gamma	X-HCg	XCg
C6	-H6AB	Cg7	[1565.01]	2.99	-2.84	18.42	136	3.757(3)

[ 1565] = X,1+Y,Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in () in the Ring-Analysis above

Cg(I)	X	у	Z	Хо	Yo	Zo				
Cg2	0.85610(11)	0.36457(8)	0.23978(8)	11.6173(13)	5.0875(10)	2.8046(10)				
Cg3	0.43669(12)	0.31845(8)	0.55100(8)	8.5095(13)	5.5416(10)	6.4449(10)				
Cg4	0.80260(9)	-0.01270(8)	0.23738(8)	9.5866(10)	0.6125(10)	2.7766(9)				
Cg7	0.63537(12)	-0.12368(8)	0.06824(8)	6.5726(13)	-1.2453(10)	0.7982(9)				
Potential Hydrogen Bonds and Schemes										

H.Acceptor [ARU] D-H.A Res Donor---D-H H...A D...A 2.60 2.986(3) C1 0.99 103 --H1AB ..N6 [] [2665.02] 2.54 3.111(3) C1 --H1AB .F4 0.99 116' C2 --H2AB ..F2 [1555.02] 0.99 2.52 3.021(4) 111 C4 --H4 ..F1 [1655.02] 0.95 2.54 3.394(4) 149 C7 --H7AB .CI1 0.98 2.79 3.743(3) 163 [] C8 --H8AB .F1 [1555.02] 0.99 2.48 3.270(3) 136 .F2 C14 --H14C [2666.02] 0.98 2.41 3.365(3) 165 C15 .CI1 2.57 --H15A [2656.01] 0.99 3.491(2) 155 C25 0.98 2.82 138 --H25B .CI1 3.603(2) []

:: No Classic Hydrogen Bonds Found

Translation of ARU-Code to CIF and Equivalent Position Code

- $[2656] = [2_656] = 1-x,-y,1-z$
- 2665.] = [ 2\_665] = 1-x,1-y,-z 2666.] = [ 2\_666] = 1-x,1-y,1-z ſ
- [ [ 1655.] = [ 1\_655] = 1+x,y,z

Table S7. Cell cycle distribution (% cells) in the individual cell cycle phases, determined by flow cytometry with the Annexin V-FITC/PI staining of the A2780 cells treated for 24 h by the equitoxic concentrations of complexes 1-PF<sub>6</sub>, 2-CIO<sub>4</sub> and 4-PF<sub>6</sub>. Control is represented by untreated cells. Cisplatin was involved for comparative purposes.

	Concentration	G0/G1 phase	SD	S phase	SD	G2/M	SD
	[µM]	[average %]		[average %]		[average %]	
Control		56.4	0.4	24.2	0.4	19.5	0.7
1-PF <sub>6</sub>	3	47.3	1.0	21.3	0.8	31.4	1.7
2-ClO <sub>4</sub> ·H <sub>2</sub> O	3	45.3	0.8	25.8	0.7	28.9	0.3
4-PF <sub>6</sub>	50	31.4	1.8	26.8	1.4	41.9	0.9
Cisplatin	30	52.4	2.8	32.8	1.7	14.8	1.2



Fig. S1 Packing view of 1-CIO<sub>4</sub>



Fig. S2 Packing view of 2-CIO<sub>4</sub>



Fig. S3 Packing view of 4-CIO<sub>4</sub>



Fig. S4 Packing view of 5-PF<sub>6</sub>



**Fig. S5** Spectral changes of complex  $1-PF_6$  (6.95 x 10<sup>-4</sup> M) in: (1) CH<sub>3</sub>CN and (2) H<sub>2</sub>O/CH<sub>3</sub>CN solution (1:4, volume ratio) at room temperature.



**Fig. S6** Spectrophotometric titration of **2-CIO**<sub>4</sub> (8.18 x 10<sup>-4</sup> M) in H<sub>2</sub>O/CH<sub>3</sub>CN solutions (curve #, volume ratio) with increasing water contents: 1, 0/5 (black); 2, 0.30/5 (red); 3, 0.50/5 (blue); 4, 0.70/5 (turquoise); 5, 1.0/5 (purple) at room temperature.



**Fig. S7** Spectral changes of complex  $4-PF_6$  (8.21 x 10<sup>-4</sup> M) in: (1) CH<sub>3</sub>CN, (2) H<sub>2</sub>O/CH<sub>3</sub>CN (0.2:4.8) and (3) H<sub>2</sub>O/CH<sub>3</sub>CN (0.4:4.6) solution (v:v ratio) at room temperature.



**Fig. S8** The ESI-MS spectra of samples containing the  $[Cu(L^1)CI]PF_6$  (**1-PF**<sub>6</sub>) (panel **A**), mixture of (1) at 10 µM and 290 µM L-Cys after 60 h of interaction (panel **B**), mixture of (1) at 10 µM and 290 µM GSH after 60 h of interaction (panel **C**).



**Fig. S9** The ESI-MS spectra of samples containing the  $[Cu(L^2)CI]CIO_4$  (**2-CIO**<sub>4</sub>) (panel **A**), mixture of (2) at 10 µM and 290 µM L-Cys after 60 h of interaction (panel **B**), mixture of (2) at 10 µM and 290 µM GSH after 60 h of interaction (panel **C**).





Fig. S10 Solid IR spectrum of L<sup>1</sup>.



Fig. S11 ESI-MS of L<sup>1</sup> in MeOH.





Fig. S12 <sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of L<sup>1</sup> in DMSO-*d*<sub>6</sub>



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Fig. S13 Solid IR spectrum of L<sup>3</sup>.



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### Fig. S14 Solid IR spectrum of L<sup>4</sup>.



Fig. S15 ESI-MS of L4 in MeOH



Fig. S16 <sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of  $L^4$  in DMSO- $d_6$ 

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Fig. S17 Solid IR spectrum of L<sup>5</sup>.





Fig. S18 ESI-MS of L<sup>5</sup> in MeOH



Fig. S19 <sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of L<sup>5</sup> in DMSO-d<sub>6</sub>





Fig. S20 Solid IR spectrum of complex 1-PF<sub>6</sub>.



Fig. S21 Electronic spectrum of complex 1-PF<sub>6</sub> (4.652 x 10<sup>-3</sup> M) in acetonitrile.



Fig. S22 Solid IR spectrum of complex 1-CIO<sub>4</sub>.



Fig. S23 ESI-MS of complex 1-CIO<sub>4</sub> in CH<sub>3</sub>CN.



Fig. S24 Electronic spectrum of complex  $1-CIO_4$  (2.036 x 10<sup>-3</sup> M) in CH<sub>3</sub>CN.



Fig. S25 Solid IR spectrum of complex 2-CIO<sub>4</sub>.



Fig. S26 ESI-MS of complex  $2-CIO_4$  in  $CH_3CN$ .



Fig. S27 Electronic spectrum of complex 2-CIO<sub>4</sub> (9.640 x 10<sup>-3</sup> M) in CH<sub>3</sub>CN.



Fig. S28 Solid IR spectrum of complex 3-PF<sub>6</sub>.



Fig. S29 Electronic spectrum of complex  $3-PF_6$  (1.655 x 10<sup>-3</sup> M) in CH<sub>3</sub>CN.



Fig. S30 Solid IR spectrum of complex 4-CIO<sub>4</sub>.



Fig. S31 Electronic spectrum of complex  $4-CIO_4$  (7.085 x 10<sup>-3</sup> M) in CH<sub>3</sub>CN



Fig. S32 Solid IR spectrum of complex 5-PF<sub>6</sub>.



Fig. S33 ESI-MS of complex 5 in  $CH_3CN$ 



Fig. S34 Electronic spectrum of complex  $5-PF_6$  (4.411 x 10<sup>-3</sup> M) in CH<sub>3</sub>CN