Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Preparation of Multi-functional Type Coordination Compounds: Spanning the quantitative restriction of Oxidizing Groups

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Experimental Section

Caution!

Since the target compound we reported is very dangerous, we should be highly vigilant when synthesizing and using it. Since violent explosion occurred during the characterization of the target compound, it is recommended that all operators should protect the test instrument when repeating our work. If some scholars repeat our work, such as the preparation of ligands and complexes, it is recommended that operators strictly follow our description, because these conditions are obtained after our repeated research. In the preparation, testing and other operations, it must be accompanied by professionals. Non-professionals are advised not to carry out this work because of the potentially dangerous. All operations must be carried out in specially customized equipment, which should have a good protective effect.

Materials and Equipment

During the experiment, the reagents (analytical grade) used were purchased from Aladdin and Azov and used without further purification. Single crystal X-ray diffraction data was collected by using Rigaku supernova single X-ray diffractometer area detector ($Mo_{K\alpha'}$, 0.71073 Å). Powder X-ray diffraction (PXRD) data of the product was tested using a Bruker D8 ADVANCE X-ray powder diffractometer ($Cu_{K\alpha'}$, 1.5418 Å). The thermal behavior of the compound was analyzed by differential scanning calorimeter (TGA/DSC2, METTLER TOLEDO STAR ^{e} system), with the heating rate was 5 K·min^{-1}, and the gas atmosphere was N_2. Infrared (IR) spectra were measured on a Nicolet Is10 spectrometer (Equipped with KBr discs) with a measurement range of 4000 - 400 cm $^{-1}$. Elemental analyses (C,H,N or C,H,N,S) were carried out on an elemental analyzer (Vario EL Cube, Germany). The mechanical sensitivities (including impact sensitivity and friction sensitivity) of the material were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 10 kg. The constant pressure reaction heat is measured by High Pressore Oxygen Calorimeter (BCA$^{@}$ 500), with the standard molar combustion enthalpy can be converted by the combustion equation. The experimental density is obtained by the powder densitometer test (Micromeritics AccuPyc II 1340). The morphologies and surface appearance of the samples were characterized using field emission scanning electron microscopy (FESEM, S-4800, Hitachi). The laser performance test is measured by Diode Laser (Changchun laser technology co., LTD. LR-ISP-980/1~1000mW. Spectral Line width (nm): < 3, Output Power (mW): 1~1000, Beam Diameter at Aperture (mm): 5.0 x 5.0, Modulating Repetition: 100KHz TTL / 10KHz Analogue. Operating parameters: theoretical maximal output power $P_{\max} = 30.15$ W; theoretical pulse length $\tau_{\max} = 49571$ μs. wavelength $\lambda = 915$ nm. Frequency F = 1Hz.).

Synthesis of AMPZCA

Drop hydrazine hydrate (0.25 mmol, 80%) into the reaction bottle, then add solid powder ethyl 5-amino-1-methylpyrazole-4-carboxylate (0.1 mmol) slowly under stirring. Then react at room temperature until the powder being dissolved (about 10-15 min). Then, the temperature was raised to 120 °C at the rate of 10 °C min^{-1}, and refluxed for 10 h. After the reaction was completed, cool to room temperature and store the whole reaction solution in the refrigerator overnight, a large number of white target products **AMPZCA** can be obtained.

Yield: 87 %. IR (KBr, ν/cm^{-1}): 3369(s), 3300(m), 3197(m), 1615(s), 1560(s), 1493(s), 1454(s), 1314(s), 1266(m), 1235 (m), 942(m), 798(m), 692 (m). MS (ESI), m/z: 154.03 [$C_5H_8N_5O^-$]. Elemental analysis (%) for $C_5H_9N_5O$ (Mr = 155.08 g mol^{-1}): calcd. C 38.7, H 5.9, N 45.1; found C 38.3, H 5.6, N 45.8. ^{1}H NMR (400 MHz, DMSO-*d$_6$*): δ 3.5 (s, 3H), 4.2 (s, 2H), 6.1 (s, 1H), 7.6 (s, 2H), 8.9 (s, 1H).

Synthesis of ECCs-1

The ligand (10mmol) was suspended in 5 ml water and heated to 40 °C. Then add $HClO_4$ slowly until the solution became clear. Then $Cu(ClO_4)_2$ solid (10 mmol) and 20 ml ethanol were added, and the reaction solution was heated to 70 °C. Continue to stir for 10 min and filter while hot. Put the filtrate in the fume hood and volatilize slowly, the blue crystals can be obtained after 1-2 d.

Yield: 76 %. IR (KBr, ν/cm-1): 3439(m), 3350(m), 3260 (m), 1651 (s), 1612 (m), 1571(m), 1244(s), 1069(s), 776(m). Elemental analysis (%) for $C_{10}H_{24}Cl_4CuN_{10}O_{20}$ (Mr = 809.73 g mol^{-1}): calcd. C 14.8, H 3.0, N 17.3; found C 14.5, H 3.2, N 17.4.

Oxygen bomb calorimetry

The constant pressure reaction heat ($\Delta_C U$) of **ECCs-1** was measured by an oxygen bomb calorimeter, and the average value was obtained by three measurements independently. The standard molar combustion enthalpy ($\Delta_C H^{\theta}{}_m$) can be obtained from the constant pressure reaction heat ($\Delta_C U$) according to the equation 1. According to the principle of Hess' law, the complete combustion reaction equations were shown in equation **1** to **4**, and the standard molar generation enthalpy ($\Delta_f H^{\theta}{}_m$) can be obtained based on the formulas **1** and **2** [CO_2(g): -393.51 kJ mol^{-1}; $CuCl_2$(s): -220.1 kJ mol^{-1}; HCl(g): -92.31 kJ mol^{-1}; H_2O(l): -285.85 kJ mol^{-1}]. The final experimental results showed that he standard molar enthalpy of formation ($\Delta_f H^{\theta}{}_m$) of **ECCs-1** were -220.6 kJ mol^{-1} and -130.7 kJ mol^{-1} respectively.

$$\Delta cH^{\theta}m = \Delta cU + \Delta nRT \tag{1}$$

Δ_n = n_g(products)-n_g(reactants), (n_g is the sum of the total moles of gas in the product or reactant, R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K)

$$\Delta_f H^{\theta}m(compound) = \sum \Delta_f H^{\theta}m(products) - \Delta_c H^{\theta}m(compound) \tag{2}$$

$$C_{10}H_{24}N_{10}O_{20}CuCl_4(s) + 5.5O_2(g) = 10CO_2\,(g) + 11H_2O(l) + 5N_2(g) + CuCl_2(s) + 2HCl(g) \tag{3}$$

Theoretical simulation based on K-J equations

The constant pressure reaction heat (ΔCU) of ECCs-1 was measured by an oxygen bomb calorimeter, Detonation speed (D) and explosion pressure (P) are the main indicators for measuring energetic materials. The various detonation characteristics of the ECCs were predicted using the modified Kamlet-Jacbos (K-J) equations (eq 5-7) which is a commonly used equation for predicting the detonation velocity and pressure of high energy materials.

$$C_{10}H_{24}N_{10}O_{20}CuCl_4(s) = 9CO(g) + 10CO_2(g) + 11H_2O(l) + 5N_2(g) + CuCl_2(s) + 2HCl(g) + C(s) \quad (4)$$

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (5)$$

$$P = 1.55\rho^2 NM^{1/2}Q^{1/2} \quad (6)$$

$$Q = \frac{-[\Delta H_f(\text{detonation production}) - \Delta H_f(\text{explosive})]}{\text{formulaweightof explosive}} \quad (7)$$

D: detonation velocity, km s-1); P: detonation pressure, GPa; ρ: density, g cm^{-3}; ΔHf: heat of formation, kJ mol^{-1}); Q: heat of detonation, J g^{-1}); N: moles of detonation gases per gram of explosive, mol g^{-1}); M: average molecular weight of gases, g mol^{-1})

Hot needle (HN) tests

Approximately 1-2 mg of the compound was dispersed on the operating table in a powdered state. The tiny iron needle is heated, and then slowly approached the compound, while recording the deflagration process of the compound with a high-speed camera.

Laser performance test

Weigh 2 mg testing samples, a total of 5 parts, and place them in sample tubes. Use a semiconductor laser to trigger the sample. Determine the minimum trigger energy by adjusting the action time and power. Take the average value as the final test value.

Detonation initiation

The test device used to breakdown of the lead plate, the material inside can be divided into two parts: the first part is filled with **ECCs-1** (30mg, pressure of fixation is 25 MPa); the second component is RDX or **ECCs-1** (300 mg, charge pressure is 40 MPa).

Theoretical decomposition mechanism study

All the structures are optimized under the level of M06-2X with the basis set of def2tzvp in Gaussian 16 package. The optimized structures are summarized in **Fig. S6**, and the discussions of Wiberg bond index and Mayer bond order (MBO) are performed at the same theoretical level in Multiwfn 3.7 program. Based on the gas-phase structures, we build 30 × 30 × 30 Å boxes for all the molecules in order to understand the stabilities and the decomposition pathways with a raised temperature by applying CPMD (Car-Parrinello Molecular Dynamic) methods. All the dynamic calculations are performed with Quantum Espresso 6.0 package. The time step is set as 4.0 a.u (~ 0.1 fs) for all complexes in the simulations. The kinetic energy cutoff for wave functions is 40 Ry (544 eV) with the effective electron mass of 600 D0 for **ECCs-1**. The PBE exchange-correlation functional is chosen, and core electrons are taken into account using PBE-type ultrasoft pseudopotentials, with valence states Cu($3d^9 4s^2$), C($2s^2 2p^2$), N($2s^2 2p^3$), O($2s^2 2p^4$), Cl($3s^2 3p^5$) and H($1s^1$) used to describe the valence electrons. In the simulation of CPMD, the time of simulation is set as 1.93 ps (20000 steps). An NVT ensemble is employed and the external temperature directly increased to 1500 K with the step of 0.1 fs. The oscillation frequency of the Noṡe thermostat is set as 550 ~ 750 THz. The simulation curves of time (step) - potential energy (a.u) relationship are showed in **Fig. S7**.

Supplementary Figures S1-S7

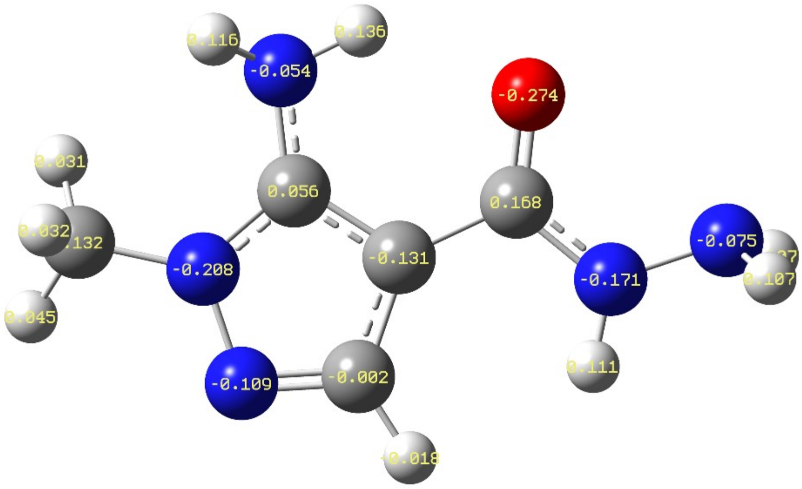

Figure S1. Atomic charge analysis of **AMPZCA**.

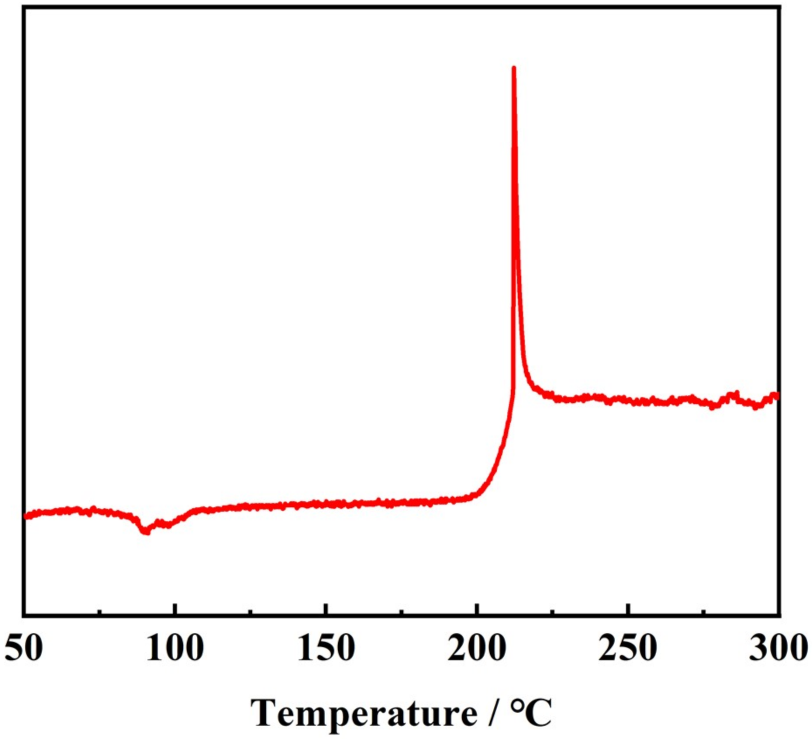

Figure S2. DTA curves of **ECCs-1**.

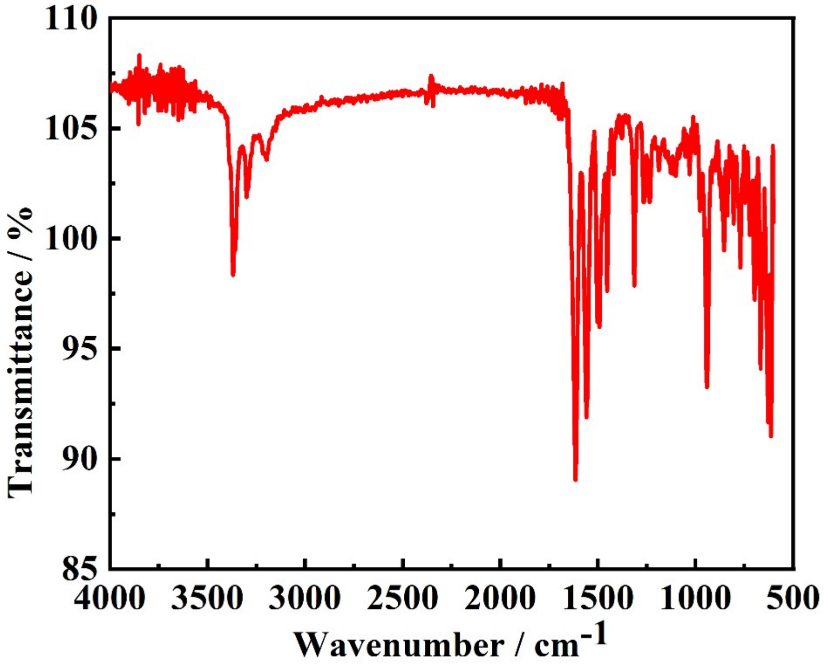

Figure S3. Infrared spectra of **AMPZCA.**

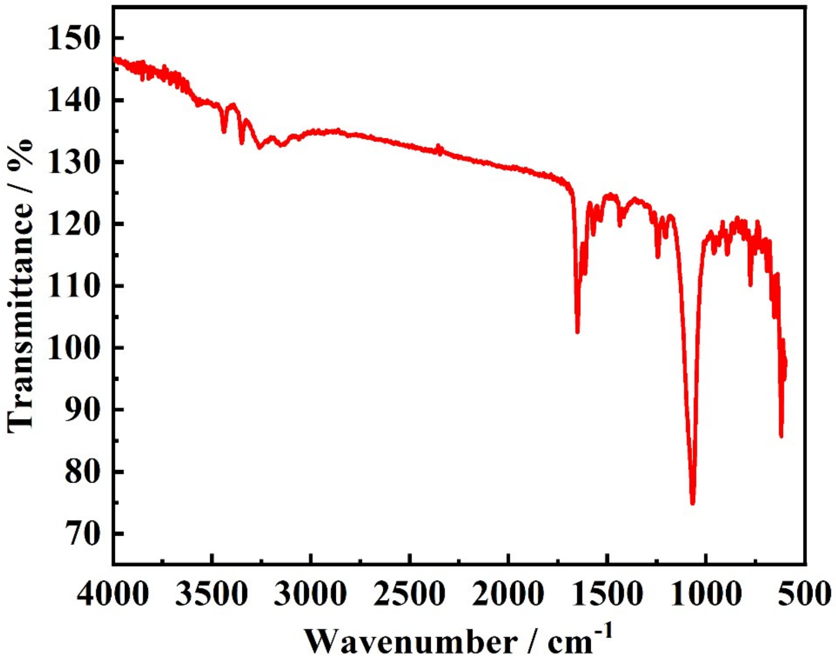

Figure S4. Infrared spectra of **ECCs-1.**

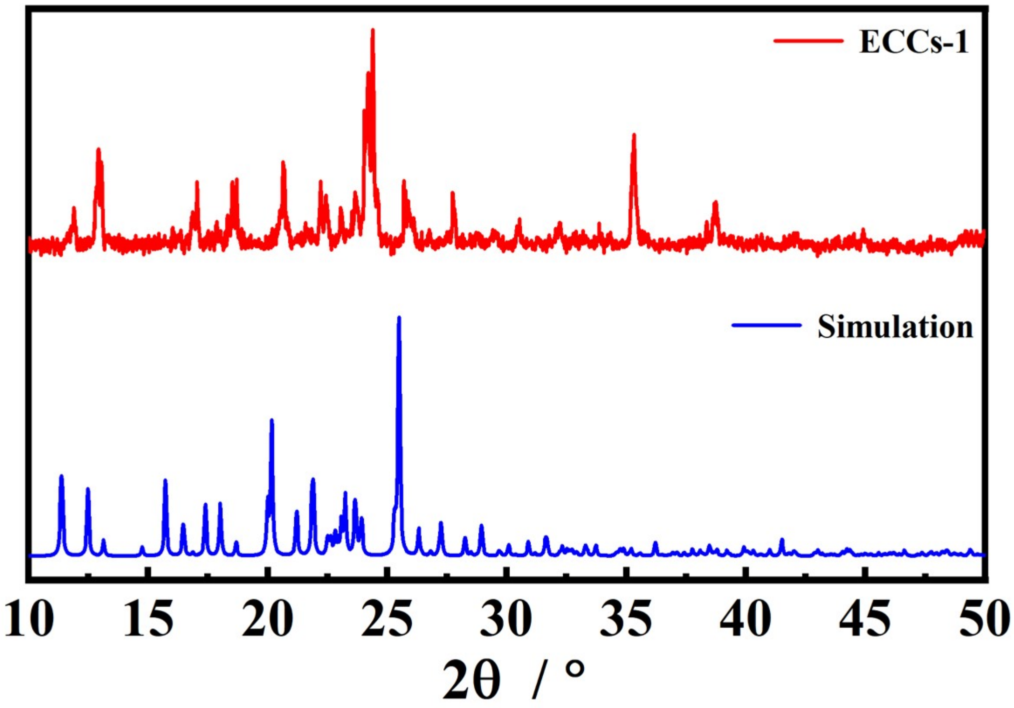

Figure S5. Comparison of single crystal and powder X-ray diffraction of **ECCs-1**.

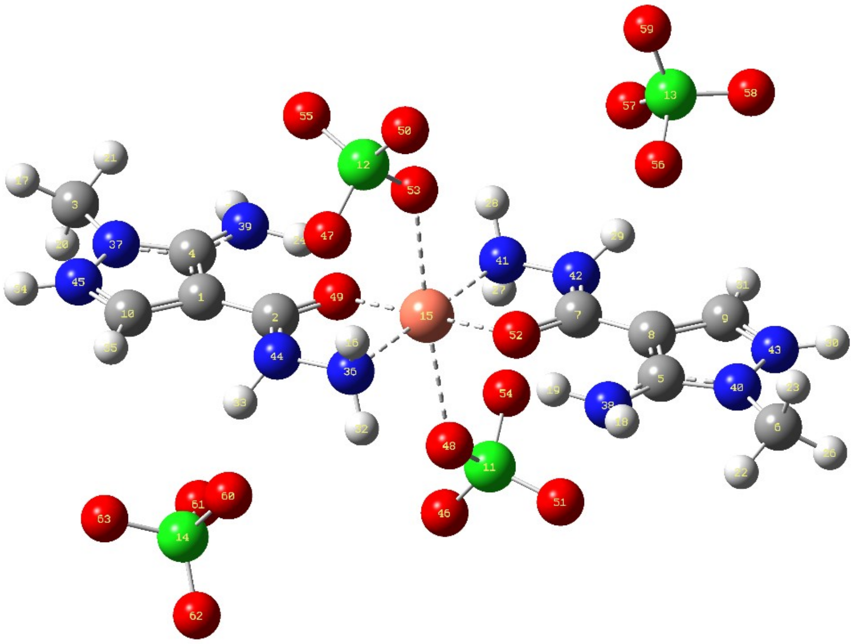

Figure S6. The optimized structure of **ECCs-1**.

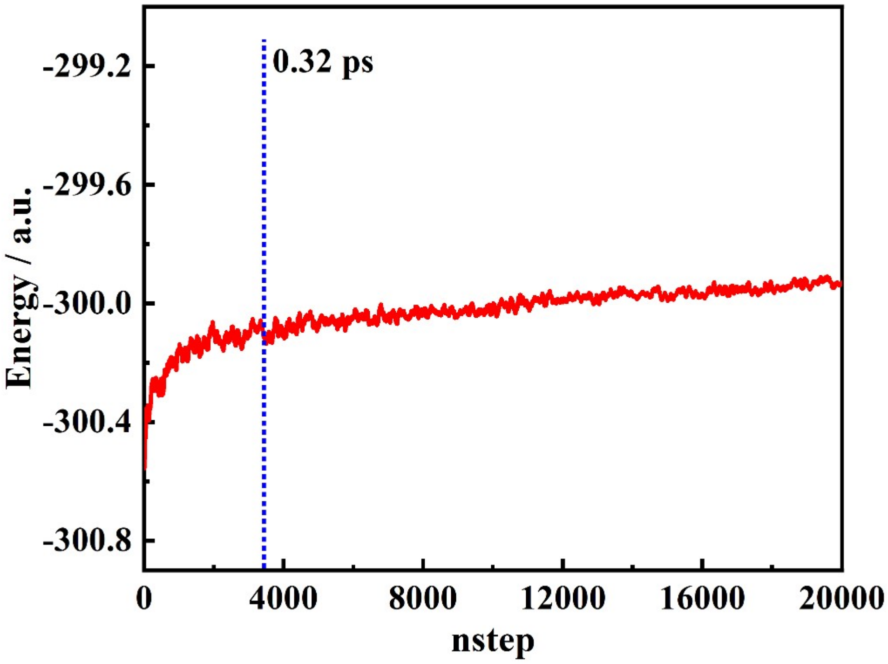

Figure S7. The simulation curves of time (step)-energy (a.u) relationship are showed

Supplementary Table S1 – S2

Table S1. Crystallographic data for **ECCs-1**

Formula	$C_{10}H_{24}Cl_4CuN_{10}O_{20}$
Temperature [K]	298.15
M_w[g mol^{-1}]	809.73
Crystal size [mm^3]	0.33 x 0.18 x 0.15
Crystal system	triclinic
Space group	*P*-1
unit cell dimensions	a= 8.2915 Å, b= 8.7114 Å, c[Å]= 11.4093 Å
	α[Å]= 108.678, β[Å]= 97.2800, γ[Å]= 105.997(3)
V[[Å^3]	729.25(12)
Z	1
ρ_{calc}[g cm^{-3}]	1.844
μ[mm^{-1}]	1.216
F(000)	411.0
2θ range[°]	5.24 – 50.04
Reflections collected	3701
Index ranges	$-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-9 \leq l \leq 13$
R_{int}	0.0275
Data/restraints/parameters	2533 / 126 / 229
Final R index [$I > 2\sigma(I)$]	R1 = 0.0568, wR2 = 0.1615
Final R index [all data]	R1 = 0.0650, wR2 = 0.1686
GOF on F^2	1.080
CCDC	2220551

Table S2. The atomic coordination of **ECCs-1.**

Atom	coordination			Atom	coordination		
	x	y	z		x	y	z
Cu1	2.2225	2.0793	5.2515	N3	1.7772	4.7065	1.2803
Cl1	1.9671	5.1285	7.2065	H3A	1.3527	5.0358	0.6081
N1	0.8208	-1.9822	9.6081	H3B	1.4175	4.0851	1.7519
N2	-0.4318	-2.1608	9.0682	N4	4.5125	3.4603	4.5709
H2	-1.013	-2.7272	9.3529	H4	5.2854	3.8372	4.573
N3	2.6678	-0.548	9.2226	N5	4.1439	2.513	5.5687
H3A	3.0922	-0.8772	9.8948	H5A	4.6498	1.7717	5.5004
H3B	3.0275	0.0734	8.751	H5B	4.2562	2.8629	6.391
N4	-0.0676	0.6982	5.9321	O1	2.4819	3.1543	3.6225
H4	-0.8404	0.3214	5.93	O2	2.7208	-0.2652	4.5415
N5	0.3011	1.6455	4.9343	O3	3.5909	-0.6995	2.4083
H5A	-0.2048	2.3869	5.0025	O4	1.2466	-0.398	2.7171
H5B	0.1888	1.2956	4.1119	O5	2.3347	-2.3484	3.508
O1	1.9631	1.0042	6.8805	C1	5.0591	5.5023	2.444
O2	1.7241	4.4238	5.9615	H1	5.8326	5.4393	2.9555
O3	0.8541	4.858	8.0946	C2	3.9093	4.7494	2.6215
O4	3.1984	4.5566	7.7858	C3	2.9982	5.1654	1.5912
O5	2.1103	6.5069	6.9949	C4	3.6024	3.7413	3.6246
C1	-0.6142	-1.3437	8.0589	C5	3.1471	6.908	-0.2594
H1	-1.3876	-1.2808	7.5474	H5C	2.5602	7.6056	0.041
C2	0.5357	-0.5908	7.8814	H5D	3.8965	7.2958	-0.7184
C3	1.4468	-1.0068	8.9117	H5E	2.6732	6.3256	-0.857
C4	0.8426	0.4172	6.8784	Cl2	-2.4368	2.2022	8.8992
C5	1.2979	-2.7495	10.7623	O6	-3.0381	3.1679	9.9043
H5C	1.8848	-3.4471	10.462	O7	-2.0092	3.1153	7.8152
H5D	0.5485	-3.1372	11.2213	O8	-1.3223	1.6044	9.4327
H5E	1.7717	-2.167	11.36	O9	-3.2892	1.3159	8.2217
Cl1	2.4779	-0.9699	3.2964	O10	-1.2445	4.238	5.4353
N1	3.6242	6.1408	0.8948	H10C	-0.4025	4.3195	5.5182
N2	4.8768	6.3194	1.4347	H10D	-1.5503	3.8932	6.1505
H2	5.458	6.8858	1.1501				