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#### Research paper

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Observation of an anion…anion interaction in a square planar copper(II) Schiff base complex: DFT study and CSD analysis

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#### Abstract

A centrosymmetric square planar bis-ligand copper(II) complex,  $[Cu(HL)_2](ClO_4)_2$ , with a potential tetradentate Schiff base, HL=2-(2-(ethylamino)ethyliminomethyl)-6-ethoxyphenol, containing pendant side arm, has been prepared and characterized by elemental and spectral analysis and single crystal X-ray diffraction studies. The potential tetradentate Schiff base is trapped in its zwitterionic form and shows a bidentate bonding mode. Several weak forces like hydrogen bonding and C-H··· $\pi$  interactions lead to the formation supra-molecular architecture. The existence of an anion-··anion interaction between the perchlorate anions have been analyzed

using DFT calculations, the Bader's theory of atoms-in-molecules (AIM) and the noncovalent interaction index (NCI plot). The O···O distance is 2.848(2) Å.

**Key words:** Copper(II); Zwitterionic Schiff base; anion…anion interactions; DFT calculations, CSD search.

#### **1. Introduction**

Schiff base ligands have been focused as attractive topic in inorganic chemistry due to their simple synthesis; versatility and their wide range of chelating ability with several transition and non-transition metal ions [1-5]. The metal ion in such complexes is usually coordinated by the iminic nitrogen atom and other donor atoms in the Schiff base molecules. Many such Schiff base complexes may be used in photochromism [6], non-linear optics [7], magnetism [8]. They may also reversibly bind oxygen in epoxidation reactions and may be used as catalyst in hydrogenation of olefins [9]. The complexes also have several biological applications [10-15]. There are examples of several metal Schiff base complexes where one or more donor arms of the Schiff bases remain as pendant [16-18]. The term pendant ligand is applied to a potential polydentate ligand having additional donor groups in its periphery. These ligands are frequently used in enzyme simulations [19] and in magnetic resonance imaging reagents [20]. They are useful for carrying a suitable radionuclide into a target cell [21]. Elaborate investigation regarding their structure/reactivity correlation is also a very important topic of today's research [22,23]. This structural ornamentation is a very significant one with the potential to influence the future development in chemistry for their ability to coordinate metal ions at additional coordination sites in competition with other reactants present in the reaction mixture. At the

same time, these non-labile set of pendant donor atoms may also be used as attachment points for other molecules leading to the formation of interesting structural motif [24].

On the other hand, copper is one of the most important elements for laboratory and industrial use and also in the field of biological systems [25-29]. Copper(II), being a d<sup>9</sup> system, prefers to undergo strong Jahn–Teller distortion, leading to an elongated octahedral or square pyramidal or finally square planar geometry. The structures and functions of many copper containing proteins (e.g. hemocyanin, plastocyanin, etc) and enzymes (e.g cytochrome c oxidase, ceruloplasmine, amine oxidases, superoxide dismutase etc) have been resolved by several researchers [30-34]. These structures contain many different ligand donor atoms (e.g. nitrogen, oxygen, sulfur) coordinated to the copper(II) centers with a variety of coordination numbers. The influence of the number of coordinating atoms around copper(II) center in the structure and function of copper containing metalloproteins and metalloenzymes is a very interesting topic of research now-a-days [35-38].

In the present work, we have trapped one potential tetradentate Schiff base in its zwitterionic form as a copper(II) complex. Zwitterionic compounds are important in the sense that they are used in the treatment of rheumatoid arthritis, other inflammatory joint diseases such as ankylosing spondylitis and psoriatic arthritis, cancer therapy, and in general as antineoplastic agents [39-42]. Zwitterionic ligands are also used to transport metal salts by coordinating both the metal cation and its attendant anions [43,44]. In our copper(II) complex of a potential tetradentate Schiff base, only two donor sites of the ligand are utilized to coordinate copper(II) and the remaining two potential donor sites are kept pendant. Herein, we would like to report the synthesis, structure and self assembly of a copper(II) Schiff base complex with a pendant ligand. One interesting feature of this compound in the solid state is the existence of O···O interactions

between the perchlorate anions. The O····O interaction has been analyzed using DFT calculations and also the noncovalent interaction plot (NCI plot) computational tool revealing the crucial role of the cationic ammonium groups in the pedant arms stabilizing the counterintuitive O····O interaction. We have also inspected the Cambridge structural database to assess whether these contacts could be a generally occurring interaction within crystal structures.

#### 2. Experimental

All starting materials and solvents were commercially available, reagent grade, and used as purchased from Sigma-Aldrich without further purification.

Caution!!! Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care.

#### 2.1. Preparations

#### 2.1.1 Preparations of [Cu(HL)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

A methanol solution of 3-ethoxysalicylaldehyde (1 mmol, 0.166 g) and N-ethyl-1,2diaminoethane (1 mmol, 0.105 mL) was refluxed for 1 h to prepare a tetradentate Schiff base 2-(2-(ethylamino)ethyliminomethyl)-6-ethoxyphenol (HL). Schiff base was not isolated and was used directly for the preparation of the complex. A methanol solution of copper(II) perchlorate hexahydrate (1 mmol, 0.370 g) was added to the methanol solution of the Schiff base and refluxed for 1 h. X-ray quality single crystals of the complex were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 520 mg (71%). Anal. Calc. for  $C_{26}H_{40}C_{12}CuN_4O_{12}$  (FW 735.06) : C, 42.48; H, 5.48; N, 9.65 Found: C, 42.4; H, 5.3; N, 9.7 % IR (KBr, cm<sup>-1</sup>): 1623 ( $\upsilon_{C=N}$ ), 2990-2869 ( $\upsilon_{CH}$ ), 3191,3143 ( $\upsilon_{NH}$ ), 1120-1045 ( $\upsilon_{ClO4}$ ); UV-Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (acetonitile), 273 ( $8.9 \times 10^4$ ), 336 ( $3.0 \times 10^3$ ), 635 ( $1.07 \times 10^2$ ).

#### 2.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin–Elmer 240C elemental analyzer. Infrared spectrum in KBr (4500-500 cm<sup>-1</sup>) was recorded using a PerkinElmer FT-IR spectrum two spectrometer. Electronic spectrum in acetonitrile (800–200 nm) was recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. The powder XRD data was collected on a Bruker D8 Advance X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2 $\theta$  range of 5-50° using 1-D Lynxeye detector at ambient conditions.

#### 2.3. X-ray crystallography

Single crystal of the complex having suitable dimensions, was used for data collection using a Bruker D8 QUEST area detector equipped with graphite-monochromated Mo Ka radiation ( $\lambda = 0.71073$  Å) at 100 K. The molecular structure was solved using the SHELX-14/7 package [45]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to nitrogen were located by difference Fourier maps and were kept at fixed positions. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Data were corrected for absorption effects using the multi-scan method (SADABS) [46]. A summary of the crystallographic data is given in Table 1.

#### 2.4. Hirshfeld Surface Analysis

Hirshfeld surfaces [47-49] and the associated two-dimensional (2D) fingerprint [50-52] plots were calculated using Crystal Explorer, [53] with bond lengths to hydrogen atoms set to standard values [54]. For each point on the Hirshfeld isosurface, two distances,  $d_e$  (the distance from the point to the nearest nucleus external to the surface) and  $d_i$  (the distance to the nearest nucleus internal to the surface), are defined. The normalized contact distance ( $d_{norm}$ ) based on  $d_e$  and  $d_i$  is given by

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vwd}} + \frac{(d_e - r_e^{vdw})}{r_e^{vwd}}$$

where  $r_i^{vdW}$  and  $r_e^{vdW}$  are the van der Waals radii of the atoms. The value of  $d_{norm}$  is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations. The parameter  $d_{norm}$  displays a surface with a red-white-blue color scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [55] and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

#### 2.5. Theoretical methods

The calculations of the noncovalent interactions were carried out using the Turbomole 7.0 [56] and the M06-2X/def2-TZVP level of theory. To evaluate the interactions in the solid state, we have used the crystallographic coordinates. The interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. The

interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique [57]. The Bader's "atoms-in-molecules" analysis has been performed at the same level of theory, using the AIMAII program [58]. The NCI plot is a visualization index based on the electron density and its derivatives, and enables identification and visualization of non-covalent interactions efficiently [59]. The isosurfaces correspond to both favorable and unfavorable interactions, as differentiated by the sign of the second density Hessian eigenvalue and defined by the isosurface color. NCI analysis allows an assessment of host–guest complementarity and the extent to which weak interactions stabilize a complex. The information provided by NCI plots is essentially qualitative, i.e. which molecular regions interact. The color scheme is a red-yellow-green-blue scale with red for  $\rho_{cut}^+$  (repulsive) and blue for  $\rho_{cut}^-$  (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively [60].

#### 2.6. CSD search

To give experimental evidence for the existence of O···O interactions between perchlorate anions in the solid state we have used the Cambridge Structure Database (CSD) since it is a big depot of geometrical information. The CSD version 5.39 (including two updates) was inspected using ConQuest version 1.21 for X-ray structures with uncoordinated ClO<sub>4</sub><sup>-</sup> anions. We selected those structures exhibiting intermolecular O···O distances ranging from 2.0 to 5.0 Å between two uncoordinated ClO<sub>4</sub><sup>-</sup> anions. Only no-disordered and no-polymeric good quality (R  $\leq$  0.1) single crystal structures, where all 3D coordinates had been determined, were considered. This gave a dataset containing 49,854 hits.

#### 3. Results and discussions

#### 3.1. Synthesis

The tetradentate Schiff base ligand, HL, was synthesized by the condensation of N-ethyl-1,2-diaminoethane with 3-ethoxysalicylaldehyde in 1:1 M ratio, following the literature method [61,62]. The Schiff base was not isolated and was used directly for the preparation of the complex. Addition of copper(II) perchlorate hexahydrate to the methanol solution of HL produced a deep green solution. Single crystals of the complex, suitable for X-ray diffraction, were grown from it.

It is to be noted here, the Schiff base is present in its zwitterionic form. The increased acidity of the medium due to the presence of perchlorate is responsible for the non-deprotonation of the Schiff base. The lower coordinating ability of perchlorate may be the driving force for the formation of this square planar complex of copper(II). The synthesis of the complex is shown in Scheme 1.



Scheme 1: Synthetic route of the complex

#### 3.2. Description of structure

#### 3.2.1. Description of structure [Cu(HL)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>

It crystallizes in monoclinic space group  $P2_1/n$ . A perspective view of the complex with selective atom-numbering scheme is shown in Figure 1 and selected bond lengths and angles are listed in Table 2. The structure determination reveals that the complex consists of a discrete centrosymmetric mononuclear cationic unit  $[Cu(HL)_2]^{2+}$  along with two non-coordinated perchlorate anions. The copper(II) centre displays square planar coordination through two imine nitrogen atoms, N(4) and N(4)<sup>a</sup> and two phenoxo oxygen atoms, O(7) and O(7)<sup>a</sup> from two zwitterionic Schiff base ligands (Symmetry transformation <sup>a</sup> = 1-x,1-y,1-z). The potential tetradentate Schiff base ligand, HL, behaves like a bidentate ligand with pendant non-coordinated ethoxy oxygen atom and protonated amine nitrogen atom.



Figure 1. Perspective view of the complex with selective atom-numbering scheme. Symmetry transformation  $a^{a} = 1-x, 1-y, 1-z$ .

The complex shows significant hydrogen bonding interactions (Figure 2). The hydrogen atom, H(1N), attached to amine nitrogen atom, N(1), forms bifurcated hydrogen bonds with the

symmetry related phenoxo oxygen atom,  $O(7)^a$  and ethoxy oxygen atom,  $O(8)^a$ . Another hydrogen atom, H(2N), attached to same nitrogen is involved in hydrogen bonding interaction with the oxygen atom, O(1') of non-coordinated perchlorate moiety. The geometric feature of hydrogen bonding interactions is given in Table 3. The complex shows inter molecular C-H··· $\pi$ interaction with C····centroid distance 3.437(3) Å. The hydrogen atom, H(13B) attached to C(13) is involved in C-H··· $\pi$  interaction with the symmetry related (2-x,1-y,1-z) phenyl ring, C(6)-C(7)-C(8)-C(9)-C(10)-C(11) of neighboring molecule, producing a supramolecular chain as illustrated in Figure 3.



Figure 2 Hydrogen bonding interactions in the complex. Symmetry transformation <sup>a</sup> = 1-x,1-y,1-

z.



**Figure 3**: Supramolecular chain in the complex created through C-H $\cdots\pi$  interactions. Selected hydrogen atoms are not shown for clarity.

#### 3.3. IR and electronic spectra

In IR spectrum of the complex, band corresponding to the azomethine (C=N) stretching vibration appears at 1623 cm<sup>-1</sup> [63]. IR spectrum of the complex exhibits two sharp bands at 3191 and 3143 cm<sup>-1</sup>, which are ascribed to the N-H stretching vibrations [64]. The bands in the range of 2990-2869 cm<sup>-1</sup> are assigned to alkyl C-H bond stretching vibrations [65]. The characteristic bifurcated absorption band for non coordinated perchlorate anions appears at 1120-1045 cm<sup>-1</sup> in the IR spectrum of the complex [66].

Electronic spectrum was recorded in acetonitrile solution in the range 200-800 nm. The complex shows intense absorption bands at short wavelengths, at 273 and 336 nm, which may be assigned to ligand to metal ion charge transfer bands (LMCT). The broad absorption band around 635 nm may be assigned to d-d transitions [67].

#### 3.4. Hirshfeld surface analysis

Hirshfeld surfaces of the complex, mapped over  $d_{norm}$ , shape index and curvedness, are illustrated in Figure 4. The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. Dominant interaction between O···H atoms can be seen in the Hirshfeld surfaces as red spots on the  $d_{norm}$  surface in Figure 4(a). Other visible spots in the Hirshfeld surfaces correspond to H. H contacts. The small extent of area and light color on the surface indicate weaker and longer contact other than hydrogen bonds. The interactions appear as distinct spikes in the 2D fingerprint plot (Figure 5). Complementary regions are visible in the fingerprint plots where one molecule acts as a donor  $(d_e < d_i)$  and the other as an acceptor  $(d_e > d_i)$ . The fingerprint plots can be decomposed to highlight particular atom pair close contacts [68]. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The proportion of O···H/H···O interaction comprises 37.7% of the Hirshfeld surfaces for each molecule. This O···H/H···O interaction also appears as two distinct spikes in the 2D fingerprint plot {Figure 5 (b)}. The upper spike corresponding to the donor spike represents the H···O interactions ( $d_i = 1.0, d_e = 1.31$ Å) and the lower spike being an acceptor spike represents the O···H interactions ( $d_e = 1.0, d_i =$ 1.31 Å) in the Fingerprint plot.



**Figure 4:** Hirshfeld surfaces mapped over  $d_{norm}$  (a), shape index (b) curvedness (c) of the complex.

**Figure 5:** Full Fingerprint plots (a) resolved into O…H/H…O contacts (b) showing the percentages of contacts contributed to the total Hirshfeld surface area of molecules of the complex.



3.5. Powder X-ray diffraction

The experimental powder XRD pattern of the bulk product of the complex is in good agreement with the simulated XRD pattern from single crystal X-ray diffraction, confirming the purity of bulk sample. The simulated patterns were calculated from the single crystal structural data (cif file) using the CCDC Mercury software. Figure 6 show the experimental and simulated powder XRD patterns of the complex.



**Figure 6:** Experimental and simulated powder XRD patterns of the complex confirming the purity of the bulk materials.

#### 3.6. Theoretical DFT study

Previous theoretical studies have suggested the possibility of finding anion-anion hydrogen-bonded cluster minima in the absence of solvent [69-75] where the existence of a dissociation barrier makes these minima stable, although their overall binding energy is repulsive [76,77]. For instance, in phosphate aggregates, the dissociation barrier can be as large as ~17 kcal/mol. Remarkably, the complex forms infinite 1D supramolecular chains in the solid state where the perchlorate anions establish intermolecular O···O contacts along the chain (see Figures 3 and 7). The O···O distance is 2.848(2) that is significantly shorter the sum of van der Waals radii (3.04 Å). Obviously perchlorate anions cannot form hydrogen bonds allowing the formation of a kinetically stable assembly. The only possible kinetically stable complex that can be envisaged is a dimer where the O atom of one  $ClO_4^-$  unit points to the Cl atom of another anion along the extension of one Cl–O bond (hypervalent  $\sigma$ -hole interaction). It should be

mentioned that several attempts have been made to optimize the perchlorate dimer at the M06-2X/def2-TZVP level of theory and even RI-MP2/def2-TZVP ab initio methods and we have been unable to locate a halogen bonded dimer as a kinetically stable stationary point. Therefore, the formation of the perchlorate dimer observed in the solid state of the complex is likely due to other factors like the presence of the ammonium groups (counter-ions) close to the anions, as further described below.



**Figure 7:** (a) Fragment of the solid state X-ray structure of the complex. H-atoms omitted for clarity. (b) Detail of the anion…anion interaction. (c) Dimerization energy of two  $[Cu(HL)_2](ClO_4)_2$  complexes. (d) Detail of the H-bonding network. Distances in Å.

In Figure 7a we show a dimeric fragment of the polymeric chain (see also in Figure 3), where the O…O interaction is highlighted. We have computed the interaction energy of the perchlorate dimer using the X-ray geometry that is repulsive ( $\Delta E_1 = +55.5$  kcal/mol), as expected due to the electrostatic repulsion between charges of the same sign. However, the dimerization energy of two [Cu(HL)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> complexes (see Figure 7c) to yield the assembly is favourable  $\Delta E_2 = -37.4$  kcal/mol, thus indicating that the additional interactions with the arms are able to

largely compensate the electrostatic repulsion from the O···O interaction. As a matter of fact, a close examination of the interaction of the perchlorate anions with the arms reveals that each  $ClO_4^-$  forms two H-bonds with the ammonium groups (see Figure 7d), one exhibiting a short distance (2.15 A) and the other one with a longer distance (2.60 Å). Those interactions, along with other van der Waals forces, compensate the electrostatic repulsion of the O···O interaction.



**Figure 8:** (a) NCI plot of the fragment of the complex. The gradient cut-off is s = 0.35 au, and the color scale is  $-0.04 < \rho < 0.04$  au. (b) Distribution of bond critical points (CPs, light blue spheres) and bond paths connecting them. The ring CPs are represented as small yellow spheres.

In order to further characterize the O···O interactions we have used two computational tools: the AIM analysis and the NCI plot index. We have performed the NCI plot using the fragment shown in the middle of Figure 8. The NCI plot enables the visualization and identification of non-covalent interactions efficiently, because it allows an assessment of host–guest complementarity and the extent to which weak interactions stabilize a complex. The representation of the NCI plot is shown in Figure 8b. It can be observed two small and bluish isosurfaces between the  $-N^+H_2$ - group and the O atom of the perchlorate thus characterizing the short H-bond. In addition, a more extended isosurfaces are located between the H atoms of the alkyl chains and the perchlorate anions thus revealing the existence of N/C–H···O interactions

that further stabilize the assembly. Finally, a green isosurface is located between the O atoms, thus suggesting a stabilizing nature of the  $O \cdots O$  interaction in this particular assembly.

In Figure 8b, the AIM distribution of critical points and bond paths have been shown. The presence of a bond critical point (CP) and bond path connecting two atoms is an unambiguous evidence of interaction [78]. The AIM analysis of the assembly reveals an intricate distribution of bond CPs and bond paths due to the existence of a large number of interactions between the anionic and the cationic parts of the assembly. A close look to the distribution reveals the existence of a bond CP and bond path inter-connecting the O atoms thus further confirming the existence of the O $\cdots$ O interaction.

Finally, the Cambridge Structure Database was inspected to evaluate if anion---anion contacts between  $ClO_4^-$  moieties might be a generally occurring interaction within crystal structures (see section 2.6 for details). Figure 9 shows some numerical data of intermolecular distance (d) between two  $ClO_4^-$  ions ranging from 2 to 5 Å. The amount of data where overlap of van der Waals shells occurs is given as percentage of the total amount of data. The fraction of van der Waals overlap ( $\leq \Sigma R_{vdw}$ ) is not negligible (1.3%) and corresponds to a total of 665 hits. In case we consider that the van der Waals overlap extends up to  $\Sigma R_{vdw} + 0.2$  Å, the fraction increases to 4.5 % corresponding to 2240 hits. These results suggest that O····O noncovalent contacts between perchlorate anions are rather common within the CSD taking into consideration the repulsive nature of the interaction.



**Figure 9**: Plot of the frequency count (%) as a function of the O···O distance (Å) for  $ClO_4^-$ ··· $ClO_4^-$  dimers. The vertical dashed blue line is added as a guide to the eye indicating the sum of the van der Waals radii. The inset numbers represent the total amount of data ( $N_{total}$ ) and the absolute and relative mount of data displaying van der Waals overlap considering only the sum of van der Waals radii ( $\Sigma R_{vdw}$ ) or losing the criterion to  $\Sigma R_{vdw} + 0.2$  Å.

Two examples selected from the CSD search commented above are shown in Figure 10, where the short  $O \cdots O$  interaction is highlighted. In detail, DUCBAG [79] structure shows a short  $O \cdots O$  contact at 2.869 Å (blue dashed line, see Figure 10a) that is stabilized by the formation of four H-bonds between the Pt-coordinated ammonia ligands and the anions. Moreover, in MULCAY [80] structure the  $O \cdots O$  interaction is evident, exhibiting an intermolecular distance that is considerably shorter than  $\Sigma R_{vdw}$ . Again the global assembly is estabilized by the formation of strong N–H···O H-bonds between the coordinated organic ligand and the perchlorate anions.



**Figure 10**. Partial views of the X-ray structure of CSD coded DUCBAG (a) and MULCAY (b). Distances in Å.

#### 4. Conclusion

The zwitterionic form of a well-known Schiff base could efficiently be trapped in a copper(II) complex. The synthesis and characterization of this new copper(II) Schiff base complex unambiguously show that a potential tetradentate Schiff base may act as a bi-dentate ligand, keeping the remaining donor sites pendant. Such structure is unprecedented for this Schiff base. Thus it opens up new possibilities for the synthesis of transition metal complex with pendant Schiff bases. Considering the novel role of pendant ligands in chemical and biological systems, the present finding may serve as a model for preparing other such complexes with pendant ligands. In the solid state, the presence of the charged pedant arms facilitates the formation of a perchlorate dimer with a close O···O contact. It has been studied by using DFT calculations and characterized using the NCI plot and AIM analyses. These type of contacts are

rather common in the CSD since around 4.5% of the structures containing perchorate present  $O \cdots O$  contacts with intermolecular distances shorter than  $\Sigma R_{vdw} + 0.2$  Å.

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#### Appendix A. Supplementary data

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No 1431250. The data can be obtained free of charge from CCDC via <u>www.ccdc.cam.ac</u>.uk/data\_request/cif.

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	Formula	$C_{26}H_{40}Cl_2CuN_4O_{12}$
	Formula Weight	735.06
	Temperature (K)	100
	Crystal system	Monoclinic
	Space group	$P2_{1}/n$
	a(Å)	8.4109(5)
	b(Å)	8.4666(5)
	c(Å)	21.7338(13)
	β	99.770(2)
	Z	2
	$d_{\rm calc} ({\rm g \ cm^{-3}})$	1.600
	μ (mm <sup>-1</sup> )	0.961
	F(000)	766
	Total Reflections	24294
	Unique Reflections	3509
	Observed data[I >2 $\sigma$ (I)]	2864
	No. of parameters	214
	R(int)	0.064
	R1, wR2 ( all data)	0.0518, 0.0839
	R1, wR2 $[I > 2 \sigma(I)]$	0.0350, 0.0775

 Table 1: Crystal data and refinement details of the complex.

Cu(1)-O(7)	1.8977(13)
Cu(1)-N(4)	1.9948(17)
O(7)-Cu(1)-N(4)	91.24(7)

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**Table 2:** Selected bond lengths and angles (°) of the complex.

Table 3: Hydrogen bond distances (Å) and angles (°) of the complex.

D-H···A	D–H	Н…А	D···A	∠D–H…A
N(1)-H(1N)····O(7) <sup>a</sup>	0.83	2.01	2.767(2)	152(2)
N(1)-H(1N)····O(8) <sup>a</sup>	0.83	2.42	3.046(2)	133(2)
N(1)–H(2N)…O(1')	0.83	2.15	2.909(2)	152(2)

D, donor; H, hydrogen; A, acceptor. Symmetry transformation <sup>a</sup> =1-x,1-y,1-z.

C

A potential tetrdentate Schiff base is trapped in its zwitterionic form in a square planar bis-ligand copper(II) complex and shows a bidentate bonding mode with pendant donor arms. The anti-electrostatic O…O inteaction between the perchlorate anions in the solid state structure

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