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In this paper, two correlation equations are established. Substituent electron effect displays important effects on the dihedral angle $\tau_1(\tau_1$ is the value of the dihedral angle between the Cu-O-N plane and O-C=N plane) and the coordinate bond length (L_{Cu-N}) in the crystal structure of the complexes.



Influence of substituents on the structure of Schiff bases Cu(II) Complexes

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Abstract: The relationship between molecular conformation and substituent effects of salicylaldehyde Schiff-base Cu(II) complexes was explored. For this study, eight samples of the complexes Cu(Sal-X)₂ (X= OMe, Me, H, F, Cl, Br, CF₃ and CN) were obtained by reaction of Cu(OAc)₂ with Schiff base ligands (Sal-X) derived from Salicydaldehyde, and their crystal structures were characterized by the X-ray diffraction technique. The QSPR methods were employed to achieve deeper insight into geometry structure of Cu(Sal-X)₂. The results show that the main geometrical parameters of Cu(Sal-X)₂ are dominated by the substituents on the aniline ring. That is, the dihedral angle τ_1 between the Cu-O-N plane and O-C=N plane increases with the increase of electron-donating effect and electron-withdrawing effect of substituents, whereas the electronic effect of substituents has the opposite effect on τ_2 , which is the dihedral angle between the aniline ring plane and C-N-Cu plane. Moreover, the bond length L_{Cu-N} decreases with growing excited-state parameter σ_{cc}^{ex} of substituents which enhances the energy of C-N bond.

Key words: Copper complexes crystal; substituent effect; dihedral angle; QSPR; bond length;

1. Introduction

Schiff bases are the popular chelating ligands, and are able to easily coordinate various metal ions ^[1-4]. Many Schiff bases metal complexes have versatile applications^[5-9] for their characteristic properties such as photochromism, magnetism, catalysis properties and remarkable biomedical activities. Some of these complexes have been reported as magnetic materials^[10], anticancer agents^[11], catalyst^[12] or energy materials^[13]. Also, a variety of metal complexes have been designed for electron transport hosts in organic light-emitting diodes (OLEDs)^[14].

It is well known that the structure dominates the properties and use of materials. Recent research ^[15] demonstrated that the steric structure and electronegativity of substituents on aniline ring of ligands had a large effect on the photophysical and electrochemical properties of the corresponding complexes. In addition, it has been reported that the electronic effect of substituents on the aniline ring has an important influence on properties of the complexes such as the chelating stability ^[16], oxidation potentials ^[17] and the reactivity ^[18]. On the other hand, molecule configuration can be fine-tuned by the substituents ^[19]. Some copper complexes exhibit the change of molecular configuration from square planar to tetrahedral coordination ^[20-22] by introduction of different substituents. It was also reported ^[23-25] that the size and nature of the substituent on the imino nitrogen of the Schiff base ligand affected the coordination geometry around copper(II) in complexes. Therefore, in order to the design of new materials for a specific purpose, we may change configuration through the substituent electronic effects.

Owing to the difficulty in cultivating single crystals of compounds, the correlation between molecular

configurations and substituents is rarely studied. Fang et al^[26-27] explored the relationship between molecular configuration and the longest wavelength maximum λ_{max} of ultraviolet absorption for Schiff bases with different substituents on the aromatic rings. A conclusion was drawn that the dihedral angle τ influenced the electronic effects of substituents on the λ_{max} , and the effect of the $sin(\tau)$ on spectroscopic properties of Schiff bases was quantified. However, up to now, the influence rule of substituents on molecular configuration of Schiff bases complexes has not been reported.

In coordination chemistry, copper complexes of Schiff bases have received considerable interest from the researchers^[28-30]. Therefore, in this work, to clarify the influence rules of substituents on molecular configuration of Schiff bases complexes, eight samples of copper complexes $Cu(Sal-X)_2$ (X= OMe, Me, H, F, Cl, Br, CF₃ and CN) was synthesized. Their crystal structures were measured experimentally, and the influence of substituents on the dihedral angle and the bond length in crystal structure was quantified.

2. Experimental methods

2.1. Sample preparation

The copper complexes $Cu(Sal-X)_2$ (1-8) were all prepared by the same methods as described in the literature [31,32], as shown in **Fig. 1**.



1-8: X=OMe, Me, H, F, CI, Br, CF₃, CN

Fig.1. Schematic representation of the Cu(Sal-X)₂ (1-8) molecules with geometrical definitions.

The Schiff-base ligands Sal-X were prepared by stirring a mixture of salicylaldehyde and corresponding substituted aniline in a 1:1 molar ratio for 20 min at room temperature. The precipitated ligands were filtered off, purified by recrystallization treatment with absolute ethanol and dried in a vacuum desiccator.

The copper complexes $Cu(Sal-X)_2$ were synthesized through a reaction between $Cu(OAc)_2$ and corresponding Schiff base ligands Sal-X. A solution of $Cu(OAc)_2$ (5 mmol) in absolute ethanol was gradually added to a solution of Schiff base ligand (10 mmol) in absolute ethanol. The mixture was heated at reflux over 4 h, and then cooled to room temperature. All the products are light brown precipitates. The crude products were filtered, washed with absolute ethanol, and finally dried in a vacuum desiccator. Suitable Crystals of the complexes **1-8** were obtained by slow evaporation from absolute ethanol. All the complexes were characterized by the single crystal X-ray diffraction.

2.2. X-ray crystallography

The structure determination of Cu(Sal-X)₂ was carried out by X-ray diffraction method^[33]. The diffraction data of the complexes were collected on a Bruker Apex-II CCD diffractometer with monochromatic Mo K α radiation ($\lambda =$

0.71073 Å) at 296(2) K, which was integrated and reduced applying SAINT with absorption and scaling correction being undertaken with SADABS program. The structure was resolved by the direct method and all non-hydrogen atoms were refined by the full-matrix least-square procedure on F^2 using SHELXL-2014 in conjunction with the Olex2 program^[34]. Anisotropic thermal parameters were designated to all non-hydrogen atoms. H atoms linked to N, C and O atoms were geometrically added and isotropically refined by the riding model. The CIF files of the crystals **1-8** were available in the Supporting Information. The partial crystallographic data for the complexes $Cu(Sal-X)_2$ (**1-8**) were summarized in the **table 1**.

Complex	1	2	3	4	5	6	7	8
Formula	$C_{28}H_{24}CuN_2O_4$	$C_{28}H_{24}CuN_2O_2$	$C_{26}H_{20}CuN_2O_2$	$C_{26}H_{18}CuF_2N_2O_2$	$C_{26}H_{18}CuCI_2N_2O_2$	$C_{26}H_{18}CuBr_2N_2O_2$	$C_{28}H_{18}CuF_6N_2O_2$	$C_{28}H_{18}CuN_4O_2$
Temp[K]	296	296	296	296	296	296	296	296
Space group	P 21/c	P 21/c	P 21/n	P -1	P 21/c	P 21/c	P b c a	R -3
Z(Z')	2	2	2	2	2	2	2	9
a(Å)	13.414(3)	12.1444(8)	11.920(3)	10.1622(14)	13.571(4)	13.828(9)	10.6858(14)	42.964(3)
b(Å)	11.167(2)	7.4760(5)	7.9269(17)	10.5001(14)	10.728(3)	10.711(7)	8.2782(12)	42.964(3)
c(Å)	7.8922(19)	13.5037(9)	12.226(3)	10.5911(13)	8.188(2)	8.203(5)	27.768(4)	3.8200(3)
α(°)	90	90	90	94.384(4)	90	90	90	90
β(°)	97.057	111.082(4)	112.154(3)	106.284(5)	98.92(2)	99.260(18)	90	90
γ(°)	90	90	90	92.239(3)	90	90	90	120
V(Å ³)	1173.2(5)	1143.96(13)	1069.9(4)	1079.4(2)	1177.7(6)	1199.3(13)	2456.4(6)	6106.6(9)
$D_{calc}(g.cm^{-3})$	1.461	1.405	1.415	1.514	1.480	1.700	1.601	1.238
$Mu(cm^{-1})$	0.969	0.983	1.046	1.056	1.180	4.268	0.965	0.834
F(000)	534	502	470	502	534	606	1196	2331
Mr	516.04	484.03	455.98	491.96	524.86	613.78	591.98	506
$R_{\rm int}$	0.0244	0.0414	0.1306	0.0471	0.0702	0.0455	0.0457	0.0761
GOF on F^2	1.036	1.022	1.047	1.014	1.102	1.090	1.127	1.088
$R_{I_{a}}^{a} w R_{2}^{b} [I > 2\sigma(I)]$	0.0261,0.0700	0.0361,0.0843	0.0482,0.1185	0.0463,0.0976	0.0716,0.1615	0.0512,0.1201	0.0661,0.1789	0.0397,0.0958
$R_{I_{a}}^{a} w R_{2}^{b}$ [all data]	0.0313,0.0739	0.0484,0.0922	0.0437/0.1133	0.0990,0.1419	0.1168,0.2126	0.0829,0.1550	0.0962,0.2183	0.0561,0.1156
$\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}} \text{ (e Å}^{-3}\text{)}$	0.273/-0.224	0.267/-0.274	0.452/-0.707	0.393/-0.654	0.540/-1.083	0.636/-0.827	0.781/-0.626	0.297/-0.398

Table 1 The partial crystallographic and experimental data for the complexes 1-8.

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3. Results and discussion

3.1. Structure description of the complexes

Single-crystal X-ray diffraction shows that the complexes are structurally similar mononuclear copper(II) complexes (**Fig. 2** for the complexes **1–8**). **Table 2** summarizes the selected dihedral angles, bond lengths and bond angles for the complexes **1–8**. Complexes **4**, **7** and **8** crystallized in the triclinic space group P-1, orthorhombic space group Pbca and rhombohedral space group R-3, respectively, while **1**, **2**, **3**, **5** and **6** all crystallized in the monoclinic space groups P21/c. The results are in good agreement with the corresponding values observed in other similar copper (II) complexes ^[35-37].

As can be seen from **Fig. 2**, there are two different molecular conformations in the crystal structure of the complex 4. For all complexes, the coordination sphere of Cu atom is found to be formed by two bidentate ligands. Each Cu atom in the complexes is four-coordinated by two imino N and two phenolic O atoms of the corresponding Schiff base ligand, forming a square-planar coordination.





Fig.2. Molecular structures of complexes Cu(Sal-X)₂ (1-8) with thermal ellipsoids set at the 50% probability.

Table 2 Selected bond lengths (Å) and angles (°) for the complexes 1-8									
	1	2	3	4	5	6	7	8	
bond lengths									
$L_{\text{Cu-O}}(\text{\AA})$	1.8829(14)	1.8793(18)	1.8773(19)	1.878(3)	1.881(4)	1.872(4)	1.886(4)	1.9139(19)	
$L_{\text{Cu-N}}$ (Å)	2.0361(14)	2.013(2)	1.9952(17)	1.995(3)	2.019(5)	2.025(4)	2.016(4)	2.045(2)	
L_1 (Å)	1.309(2)	1.300(3)	1.306(3)	1.305(5)	1.322(8)	1.319(7)	1.317(6)	1.315(3)	
L_2 (Å)	1.420(3)	1.414(4)	1.422(3)	1.414(6)	1.410(9)	1.411(7)	1.415(7)	1.419(4)	
L_3 (Å)	1.428(3)	1.434(3)	1.424(3)	1.436(6)	1.419(8)	1.420(7)	1.423(7)	1.428(4)	
L_4 (Å)	1.295(2)	1.287(3)	1.291(3)	1.293(5)	1.299(7)	1.291(7)	1.300(7)	1.296(3)	
$L_5(\text{\AA})$	1.433(2)	1.441(3)	1.442(3)	1.442(6)	1.439(7)	1.440(7)	1.430(6)	1.437(3)	
bond angles									
δ_1 (°)	90.61(6)	88.58(8)	91.54(7)	88.91(14)	89.23(19)	89.15(18)	90.95(17)	89.22(8)	
$\delta_2(^{ m o})$	124.80(12)	128.69(16)	128.21(14)	131.0(3)	126.1(4)	126.1(3)	125.3(3)	122.89(17)	
$\delta_3(^{\circ})$	121.34(12)	122.17(17)	123.15(15)	123.6(3)	122.4(4)	121.6(4)	121.7(3)	120.57(17)	
dihedral angle									
<i>τ</i> ₁ (°)	23.37	21.51	18.84	19.82	20.91	21.65	22.9	29.56	
$\tau_2(^{\rm o})$	47.97	67.77	75.97	67.49	53.6	54.08	52.34	36.14	

The letters L_1 - L_5 correspond to distances depicted in Fig. 1. The letters δ_1 - δ_3 correspond to bond angles in Fig. 1.

 τ_1 is the value of the dihedral angle between the Cu-O-N plane and O-C=N plane in Fig. 1.

 τ_2 is the value of the dihedral angle between the aniline ring plane and C-N-Cu plane in Fig. 1.

3.2. Effect of substituents on molecular conformation

To elucidate the influence of the substituent X on the aniline ring of the ligand on the peculiarities of the molecular conformation of the copper complexes, we investigated the crystal structure of the complexes. The Hammett constant σ_{p} and excited-state parameters σ_{cc}^{ex} of the substituent X were listed in **Table 3**.

Table 3 The Hammett constant σ_{p} and excited-state parameters σ_{cc}^{ex} of substituent X

X	OMe	Me	Н	F	CI	Br	CF ₃	CN
$\sigma_{_{ m p}}{}^{^a}$	-0.27	-0.17	0	0.06	0.23	0.23	0.54	0.66
$\sigma^{_{\mathrm{cc}}{}^{b}}_{_{\mathrm{cc}}}$	-0.5	-0.17	0	0.06	-0.22	-0.33	-0.12	-0.70

^{*a*}The values were taken from Reference^[38] al Pre-proof ^{*b*}The values were taken from Reference^[39,40]

In crystal structure, the dihedral angle is an important parameter to estimate planarity of a molecule. As shown in **Table 2**, the dihedral angle τ_1 between the Cu-O-N plane and O-C=N plane varies in the range of 18.84°–29.56°, while the variation range of the dihedral angle τ_2 between the aniline ring plane and C-N-Cu plane is from 36.14° to 75.97°. It should be noted that the dihedral angle is clearly affected by the substituent of the aniline ring, and that the influence regularity of substituent on them is opposite: the dihedral angle τ_2 becomes smaller as the electronic effect of the substituent increases, whereas the dihedral angle τ_1 increases with the increase of electron-donating effect and electron-withdrawing effect of the substituent X.

Then, we choose the excited-state parameter (σ_{cc}^{ex}) and Hammett parameter (σ_{p}) of substituent X attached to

aniline ring to correlate the dihedral angle τ_l . The equation (1) is obtained.

$$\tau_{1} = 19.83 + 11.19\sigma_{CC}^{ex^{2}} + 9.94\sigma_{p}^{2}$$
(1)
R=0.9857, S=0.6548, F=85.31, n=8
R_{cv}=0.9774, S_{cv}=0.6765

Where R is the correlation coefficient, S is standard deviation, F is F-statistics and n indicates the number of sample. The correlation result of equation (1) is good. As shown in equation (1), the dihedral angle τ_1 between the Cu-O-N plane and O-C1=N plane becomes bigger when the value of σ_p^2 or $\sigma_{CC}^{ex^2}$ is higher. The distortion of the Cu chelating ring increases with the increase of electron-donating effect and electron-withdrawing effect of substituents. To test the predictive ability of equation (1), we carried out the leave-one-out cross validation (LOO). Here R_{cv} and S_{cv} were the correlation coefficient and standard deviation of LOO, respectively. **Fig. 3** shows that the calculated values τ_1 (cal.) and the predicted values τ_1 (pred.) are in highly agreement with the experimental ones τ_1 (exp.).The result of LOO demonstrates good performance of equation (1).



Fig. 3 The plot of the calculated τ_1 (cal.) by equation (1) and the predicted τ_1 (pred.) by LOO versus the experimental τ_1 (exp.) for the **Cu**(**Sal-X**)₂

Bond angle is another important parameter in crystal structure. Here, we discuss the coordinate bond lengths related to the Cu atoms only. Through the comparison of bond lengths for the complexes in **Table 2**, it clearly shows that the substituent X mostly affects Cu-O and Cu–N bonds. The Cu-O bond length (L_{Cu-O}) of complexes

increases from 1.872Å to 1.914Å, while the Cu-N coordinate bond length (L_{Cu-N}) of complexes varies from 1.995Å up to 2.045Å. Thus, we attempt to carry out a correlation analysis for L_{Cu-N} , and find the correlation result of L_{Cu-N} and excited-state parameter σ_{cc}^{ex} is good. The equation (2) is established, and leave-one-out cross validation (LOO) was carried out to test predictive ability for this equation.

$$L_{Cu-N} = 2.000 - 0.097 \sigma_{cc}^{ex} - 0.046 \sigma_{CC}^{ex}^{2}$$

$$R = 0.9870, S = 0.0034, F = 94.21, n = 8$$

$$R_{cv} = 0.9733, S_{cv} = 0.0038$$
(2)

Therefore, we can conclude that the excited-state parameter σ_{cc}^{ex} of substituent X has an important effect on

the bond length (L_{Cu-N}) . Bigger σ_{cc}^{ex} value shortens the bond length (L_{Cu-N}) , and enhances the energy of Cu–N bond. As shown in Fig.4, L_{Cu-N} (cal.) and L_{Cu-N} (pred.) are in good agreement with L_{Cu-N} (exp.). What's more, the leave-one-out cross validation gave the similar results with the calculated values by equation (2). Thus, the equation (2) is reliable and has good predictive ability.



Fig. 4 The plot of the calculated $L_{Cu-N}(cal.)$ by equation (2) and the predicted $L_{Cu-N}(pred.)$ by LOO versus the experimental $L_{Cu-N}(pred.)$ for the Cu(Sal-X)₂

4. Conclusion

In this study, a series of the complexes $Cu(Sal-X)_2$ (1-8) with different substituents X=OCH₃, CH₃, H, F, CI, Br, CF₃ and CN in para-position of aniline ring, were synthesized, and eight single crystals were obtained. The influence of the substituents X on the crystal configuration of Cu(Sal-X)₂ was investigated. The Conclusions are drawn as follows:

1. The dihedral angle τ_1 between the Cu-O-N plane and O-C1=N plane varies with the substituent X. τ_1 is bigger when the value of σ_p^2 or $\sigma_{CC}^{ex^2}$ is higher. The distortion of the Cu chelating ring increases with the increase of electron-donating effect and electron-withdrawing effect of substituents. However, the substituent electronic effect has the opposite effect on the τ_2 .

2. The excited-state parameter σ_{cc}^{ex} of substituents X has an important effect on the bond length (L_{Cu-N}).

Bigger σ_{cc}^{ex} values shorten the bond length (L_{Cu-N}), and enhance the energy of C-N bond.

3. Two correlation equations between the geometrical parameters (τ_1 and L_{Cu-N}) and the substituent parameters are obtained. It is helpful to understand the influence of the substituent effect on the molecular conformation of the complex crystals, and also provides a new theoretical reference for the research of this field and the molecular design of new materials with specific properties.

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Appendix A. Supplementary data

CCDC 1909136, 1909139, 1909123, 1909141, 1909142, 1909145, 1909144 and 1909143 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www. ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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Highlights

1. Eight crystals of copper complexes with different substituents were cultivated, and the main geometrical parameters were obtained.

2. The quantitative correlation between dihedral angle τ_1 and substituent effects was obtained.

3. The quantitative correlation between the coordinate bond length (L_{Cu-N}) and excited-state

substituent parameter (σ_{cc}^{ex}) was established.

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Author Contribution Statement

Yan Xiao: Conceptualization, Methodology, Software, Validation, Visualization, Data curation, Writing- Original draft preparation.

Chenzhong Cao: Investigation, Supervision, Writing- Reviewing and Editing.

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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