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A zinc(II) complex chelated by 1,10-phenanthroline ligand: Synthesis, crystal structure and hirshfeld surface analysis

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Abstract : In this paper, the synthesis, crystal structure, BVS calculation and hirshfeld surfaces and fingerprint plots analyses of a new complex $[Zn(phen)_2(H_2O)Cl]Cl (phen = 1,10-phenanthroline)$ are reported. The X-ray structure analysis of the complex revealed the zinc ion was located in the six-coordinated octahedral geometry, consisted of four N atoms, one water molecules and a Cl atom. BVS calculation associated with crystal structure confirmed the

INTRODUCTION

Noncovalent weak intermolecular interactions, which are important contributions besides coordination bonds, have gained much attention due to their unquestionable role in various chemical, physical, and biological processes^[1-4]. Their influence on molecular aggregation is still a subject of discussions basing on experimental and theoretical techniques^[5,6]. Our group has

+2 oxidation state of the metal cations. Hirshfeld surfaces and fingerprint plots analyses indicated that besides O-H…Cl there were also C-H…Cl, C-H…O and π … π weak interactions in the complex, which linked molecules forming 1D wavy chains, then 2D layer and 3D net structure. © Global Scientific Inc.

Keywords : 1,10-phenanthroline; Zinc complex; Hirshfeld surface.

been devoting ourselves to weak interactions persistently^[7-12]. Nowadays, though some weak interactions such as the hydrogen bonds formed by C-H donors have been well-established in the crystallographers community^[13-16], it is still difficult to definitely distinguish the effect of each interaction in the architecture. Recently, in order to decompose the intermolecular interactions, the quantitative analysis of molecular crystal structures using tools based on Hirshfeld surfaces has rapidly

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gained in popularity^[17,18].

Phenanthroline and its derivatives are among the most frequently used N-heterocyclic chelating agents in inorganic chemistry^[19-25], because of their use in molecular scaffolding in supramolecular assemblies, DNA cleaving, structural studies, building blocks for synthesis of metallo-dendrimers, thin films with luminescent properties, control of redox properties, analytical chemistry, and catalysis^[26-28].

In the process of expanding researches on weak interactions, we synthetized a new complex [Zn $(C_{12}H_8N_2)_2(H_2O)CI$]Cl (1) with zinc(II) and 1,10-phenanthroline. In this paper, we report the synthesis and crystal structure of the complex, and using the CrystalExplorer software analyse the hydrogen bonds in the complex.

EXPERIMENTAL

All chemicals were of analytical reagent grade and used without further purification.

X-ray crystallography and structure solution

Single-crystal X-ray diffraction data collections of complex *1* was performed on a CCD area detector diffractometer at 298(2) K with graphitemonochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω -scan technique.

The structures were solved by direct methods with the program package^[29]. All non-H atoms were reûned anisotropically. Hydrogen atoms attached were added theoretically. The ûnal cycle of full-matrix least-squares reûnement was based on observed reûections and variable parameters. Crystallographic data of the complex *I* were shown in TABLE 1. Selected bond lengths and bond angles were given in TABLE 2.

Large void spaces were examined using the SQUEEZE procedure in PLATON^[29f], accounting in total for 1290.6 Å³ per unit cell, i.e. some 20.6% of the total volume. We have not included any solvent molecules in this model.

Hirshfeld surface

Hirshfeld surfaces^[30,31] and related graphical tools^[32,33] have been shown to enhance exploration of the nature of the interactions between molecules in crys-

tals. The Hirshfeld surface partitions crystal space into smooth non-overlapping volumes associated with each molecule, and is defined implicitly where the ratio of promolecule to procrystal electron densities equals 0.5. Since the local nature of the surface is dictated by the electron density and position of neighbouring atoms inside and outside the surface, it reflects in considerable detail the immediate environment of a molecule in a crystal, and summarizes all intermolecular interactions in a remarkable graphical fashion^[34].

Preparation of the complex

A mixture of zinc chloride (0.14g, 1.0mmol), benzoic acid (0.12g, 1.0mmol), imidazole (0.07g, 1.0mmol), 1,10-phenanthroline (0.34g, 1.0mmol), vanadium pentoxide (0.18g, 1.0mmol) and water (17ml) was sealed in 25ml Teflon-lined stainless steel reactor and heated to 453K for 48h. Colorless block crystals of the title compound suitable for X-ray analysis were obtained.

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction revealed that complex *1* crystallized in the triclinic with number 2 space group *P-1*. The molecular structure was described in Figure 1. The central Zn ion exhibited octahedron geometry, in which three N atoms (N1, N2, N3) from two phenanthroline molecules together with the coordinated water located at the equatorial plane, while the N4 and C11 occupied apical positions. Compared to the similar structure with disordered solvent molecule^[35], the length of coordination bonds were more uniform in *1*, such as Zn-O 2.119 and average Zn-N 2.193 in *1*, while 2.090 and 2.205 in ref.35, which resulted in the perfect octahedral coordination around Zn.

Here we have taken recourse to the calculation based on the bond valence sums (BVS) model^[36] to assign the oxidation state of the metal center and the surroundings of coordinated O atoms in the complex. In this method, the valence *s* of a bond between two atoms *i* and *j* is related by an empirical expression (1) where r_{ij} is the length of the bond (expressed in Å), and r_0 is a parameter characteristic of the bond.

$$S_{ij} = \exp[(r_0 - r_{ij})/0.37]$$

This r_0 , known as a bond valence parameter, is

(1)

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however geometry and coordination number specific. The oxidation number N_i of the atom *i* is simply the algebraic sum (2) of these *s* values of all the bonds (*n*) around the atom, *i*.

$$N_i = \sum_{i=1}^{n} S_i \tag{2}$$

Brese et al.^[37] had refined r_0 values for Zn(II)-O bonds as 1.704Å, Zn(II)-N bonds as 1.77Å, and Zn(II)-Cl as 2.01Å. Taking these r_0 values and equations above, the values (TABLE 4) for the zinc cation came out to be 2.01, assigned the +2 oxidation state.

TABLE 1 : Crystal data and structure refinement for 1

Complex	1
Empirical formula	C ₂₄ H ₁₈ Cl ₂ N ₄ OZn
Color/shape	colorless / block
Formula weight	514.69
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Crystal size (mm)	$0.44 \times 0.27 \times 0.26$
Space group	P-1
Unit cell dimensions	
a(Å)	9.6988 (9)
b(Å)	11.5101 (11)
c(Å)	13.1057 (13)
α(°)	64.073 (1)
β(°)	84.148(2)
γ(°)	78.830 (2)
Volume (Å ³)	1290.6 (2)
Z	2
Calculated density (mg m ⁻³)	1.324
Absorption coefficient (mm ⁻¹)	1.18
F_{000}	524
θ range for data collection	3.2~24.5
Index ranges	-11 <h<11, -12<k<13,<="" td=""></h<11,>
	0 <l<15< td=""></l<15<>
Reflections collected	4624
Independent reflections	4624 [$R_{int} = 0.0000$]
Completeness (%)	98.8
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares
	on F ²
Data/restraints/parameters	4624 /0/289
Goodness-of-fit on F^2	1.073
Final R indices $[I > 2\sigma(I)]$	R_1 =0.0376, wR_2 =0.0945
R indices (all data)	$R_1 = 0.0488, wR_2 = 0.1026$
Largest diff. peak and hole $(e \cdot Å^{-3})$	0.388 and -0.257

TABLE 2 : Selected bond lengths (Å) and angles (°) for 1

Complx 1			
Zn1-O1	2.119 (2)	Zn1-N3	2.192 (2)
Zn1-N1	2.149 (2)	Zn1-N2	2.266 (2)
Zn1-N4	2.167 (2)	Zn1-Cl1	2.3489 (9)
O1-Zn1-N1	94.65 (9)	N4-Zn1-N2	89.94 (9)
O1-Zn1-N4	94.00 (9)	N3-Zn1-N2	89.76 (9)
N1-Zn1-N4	162.54 (9)	O1-Zn1-Cl1	91.85 (6)
O1-Zn1-N3	169.08 (9)	N1-Zn1-Cl1	97.26 (7)
N1-Zn1-N3	92.98 (9)	N4-Zn1-Cl1	97.59 (7)
N4-Zn1-N3	76.65 (9)	N3-Zn1-Cl1	94.93 (7)
O1-Zn1-N2	84.55 (8)	N2-Zn1-Cl1	171.87 (7)
N1-Zn1-N2	75.83 (9)		

TABLE 3 : Hydrogen-bond geometry (Å,	°) in 1
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D-HA	d(D-H)	d(H···A)	d(D…A)	<(DHA)
Complex 1				
O1-H1B····Cl2 ⁱ	0.82	2.28	3.093 (2)	172
O1-H1A····Cl2	0.84	2.36	3.158 (2)	161
Symmetry codes:	(i) -x+1, -	y+1, -z+1.		



Figure 1 : A view of the structure of *1* with displacement ellipsoids drawn at the 30% probability level.

At the same time, calculations 0.326 for O1 also confirmed the presence of water molecule rather than hydroxyl coordinated to the metal cation.

TABLE 4 : Bond valence	e values for th	he metal cation in 1.
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Bond	Bond distance	Bond valence	Bond valance	
Complex 1				
Zn1-O1	2.119 (2)	0.326		
Zn1-N1	2.149 (2)	0.358		
Zn1-N4	2.167 (2)	0.342	2.01 for $7n$	
Zn1-N3	2.192 (2)	0.320	2.01 IOF ZII	
Zn1-N2	2.266 (2)	0.262		
Zn1-Cl1	2.3489 (9)	0.400		

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Figure 2: Molecule packing diagram for the complex *I*, a 1D chain linked by O-H…Cl (Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1)



 $\label{eq:source} Figure \ 3: Hirshfeld \ surfaces \ of the \ complex \ 1 \ mapped \ with \ d_{norm} \ property, the \ molecules \ in \ tube/licorice \ representation \ within \ the \ transparent \ surface \ maps. \ O-H^{\dots}Cl(1), C-H^{\dots}Cl(2) \ and \ C-H^{\dots}O(3)$



Figure 4 : a) C-H···Cl and C-H···O hydrogen bonds diagrams; b) π ··· π interactions in the complex 1

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Figure 5 : Fingerprint plots of the complex 1: A) O-H···Cl plus C-H···Cl; B) π ··· π and C) C-H···O weak interactions, listing the percentages of contacts contributed to the total Hirshfeld surface area of molecules

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Although the simple structure, there are interesting hydrogen bonds in the complex. Firstly, inter-molecular hydrogen bonds originating from the coordinated water molecule O and chloridion, named O1-H1B···Cl2 and O1-H1A···Cl2ⁱ (Symmetry codes: (i) -x+1, -y+1, -z+1), linked each unit forming 1D wavy chains, shown in Figure 2. The hydrogen bonds geometry are given in TABLE 3.

Using the CrystalExplorer software, we found that there are also C-H···Cl and C-H···O hydrogen bonds besides primary O-H···Cl hydrogen bonds in the complex, and the strength of different kinds of hydrogen bonds can easily be distinguished according to the area and degree of red regions from figures of hirshfeld surfaces (Figure 3). Corresponding C-H···Cl and C-H···O diagrams were shown in Figure 4a, furthermore, π - π interactions also help consolidating the crystal packing with distances between 3.5~3.7 Å (Figure 4b), and these weak interactions connected each chain to 2D layer, then 3D net structure.

The percentages of contacts contributed to the total Hirshfeld surface area of molecules are shown in the Figure 5, and the proportions of O-H…Cl plus C-H…Cl, π … π and C-H…O interactions are 15.5%, 7.2% and 1.9% respectively of the total Hirshfed surfaces for the complex *1*.

CONCLUDING REMARKS

Thus we have synthesized and structurally characterized a novel complex based on zinc(II) and 1,10phenanthroline ligand. BVS calculation confirmed the +2 oxidation state of the metal cations. Hirshfeld surface and fingerprint plots analyses indicated that the existing of weak interactions helped consolidating the crystal structure, which linked the unit forming 1D wavy chains, then 2D layer and 3D net structure.

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