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Synthesis, spectroscopic and crystal structure investigation of [Cu(bzsmp)$_2$Cl$_2$]; {bzsmp = 2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4-oxadiazole}: cyclization of N^2-[bis(benzylsulfanyl)methylene]-2-methoxybenzohydrazide to 2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4 -oxadiazole during complexation

M. Singh [a], V. Aggarwal [b], U.P. Singh [b], N.K. Singh [a,*]

[a] *Department of Chemistry, Banaras Hindu University, Varanasi 221 005, Uttar Pradesh, India*
[b] *Department of Chemistry, Indian Institute of Technology, Roorkee 247 667, Uttarakhand, India*

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ABSTRACT

The ligand N^2-[bis(benzylsulfanyl)methylene]-2-methoxybenzohydrazide (N^2-bmbh) (**1**) on reaction with CuCl$_2$.2H$_2$O yielded the mononuclear complex [Cu(bzsmp)$_2$Cl$_2$] (**2**) (2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4-oxadiazole, bzsmp). Complex **2** has been characterized by analytical, spectroscopic and X-ray data. X-ray study of **2** reveals that the cyclized ligand 2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4-oxadiazole (bzsmp) acts as neutral bidentate ligand to form six membered chelate ring and the presence of C–H···π (face to edge) and C–H···S and two type of C–H···Cl weak interactions.

1. Introduction

The 1,3,4-oxadiazoles have found applications in several areas [1,2] such as anti tuberculostatic, anti-inflammatory, analgesic, antipyretic, anticonvulsant and medicine [3–6]. The syntheses of this type of heterocyclic compounds have attracted considerable attention and a number of methods have been used for their syntheses [7–9]. The widely used strategy involves the dehydrative cyclization of diacylhydrazides usually with strong acids [10–13]. The cyclization of potassium salt of 3-benzoyldithiocarbazate into the corresponding 5-phenyl-1,3,4-oxadiazole-2-thiol was first reported by Hoggarth [14]. The cyclization of 3-acyldithiocarbazates esters, N-aroyldithiocarbazates and their salts to 1,3,4-oxadiazoles in the presence of a base is also reported in the literature [15–18]. Several other methods are reported for the synthesis of oxadiazoles from acyclic precursor which includes oxidative cyclization of acylhydrazones [19], acylthiourea [20–22] and acylthiosemicarbazides [23–26]. Platinum assisted cyclization of S-methyl 3-acyl-2-methyldithiocarbazates under mild conditions was reported by Bergamini and co-workers [27]. Earlier we have reported the metal assisted cyclization of N-benzoyldithiocarbazate to 5-phenyl-1,3,4-oxadiazole-2-thiol and potassium[N′-(pyridine-3-carbonyl) hydrazine to 5-(3-pyridyl)-1,3,4-oxadiazole-2-thione in the presence of an excess ethylenediamine (en) [28,29]. A few papers are available on the syntheses and X-ray studies of [bis(benzylsulfanyl)methylene]-2-acidhydrazide [30,31] and (benzylsulfanyl)-1,3,4-oxadiazole [32,33], but for the first time we report here the metal complex of 2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4-oxadiazole obtained from the cyclization of N^2-[bis(benzylsulfanyl)methylene]benzohydrazide (N^2-Hbmbh) during complexation. The cyclization of N^2-Hbmbh to 2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4-oxadiazole has been performed under normal condition without the use of any other reagents viz. base or acid as already described in the case of other oxadiazoles. The spectroscopic and single crystal X-ray studies of the resulting Cu(II) complex obtained by the reaction of Cu(II)chloride and N^2-[bis(benzylsulfanyl)methylene]-2-methoxy-benzohydrazide [N^2-Hbmbh] is reported in the present paper.

2. Experimental

2.1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Methyl 2-methoxy benzoate (Sigma Aldrich, USA) and hydrazine hydrate (S.D. Fine Chemicals, India) were used as such. All solvents were purchased from Merck Chemicals, India and used after purification.

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* Corresponding author. Tel.: +91 542 2318529; fax: +91 542 2368127.
E-mail addresses: nksingh@bhu.ac.in, singhnk_bhu@yahoo.com (N.K. Singh).

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2.2. Preparation of the ligand N^2-Hbmbh (**1**)

The ligand N^2-Hbmbh was synthesized as described previously [30].

2.3. Preparation of the complex $[Cu(bzsmp)_2Cl_2]$ (**2**)

A solution of N^2-Hbmbh (**1**) (2 mmol) in MeOH (15 ml) was added to a solution of $CuCl_2 \cdot 2H_2O$ (1 mmol) in 10 ml of MeOH and the mixture was stirred for 2 h at room temperature. The resulting green color solution was filtered off and kept for crystallization. Green Crystals of **2** suitable for X-ray analyses were obtained by slow evaporation of its methanolic solution over a period of 21 days. Yield 64%; m.p. 145 °C. *Anal.* Calc. for $C_{32}H_{28}N_4CuO_4S_2Cl_2$ (731.17): C, 52.57; H, 3.86; N, 7.66. Found: C, 52.42; H, 4.12; N, 7.60%. I.R. data (ν cm^{-1} KBr) ν(C═N) 1603 s; ν(C–O–C) 1254 w; ν(N–N) 1133 s; ν(C–S) 869 m; ν(CH_2) 2979; ν(Cu–N) 478, ν(Cu–O) 420, ν(Cu–Cl) 325.

2.4. Physical measurements

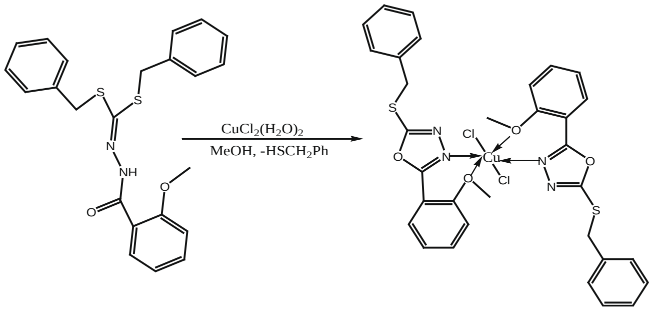
Carbon, hydrogen and nitrogen contents were estimated on a CHN Analyser Model CE-440. Magnetic susceptibility measurement was performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)$_4$] as the calibrant and electronic spectra were recorded on UV-1700 Pharmaspec spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer.

3. Crystal structure determination

The X-ray data collection and processing for **2** were performed on Bruker Kappa Apex-CCD diffractometer by using graphite monochromated Mo Kα radiation (λ = 0.71070 Å) at 273(2) K. Crystal structure was solved by direct methods. Structure solution, refinement and data output were carried out with the SHELXTL program [34,35]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. Images were created with the DIAMOND program [36]. Hydrogen bonding interactions in the crystal lattice were calculated with both SHELXTL and MERCURY [37].

4. Results and discussion

The $[Cu(bzsmp)_2Cl_2]$ [bzsmp = 2-benzylsulfanyl-5-(2-methoxyphenyl)-1,3,4-oxadiazole] was obtained by stirring the methanolic solution of N^2-Hbmbh (**1**) and $CuCl_2 \cdot 2H_2O$ in a 2:1 molar ratio at room temperature. A ring closure reaction takes place due to cleavage of C–S bond followed by elimination of $PhCH_2SH$ during complexation resulting in the formation of complex **2** (Scheme 1). The green solution obtained after the reaction was filtered off and on



Scheme 1. Preparation of complex $[Cu(bzsmp)_2Cl_2]$.

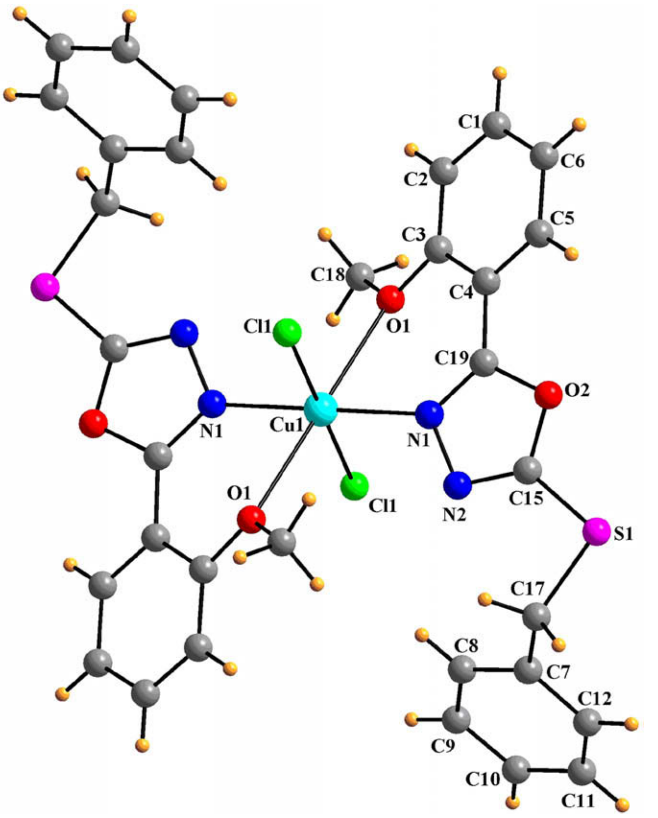


Fig. 1. Molecular structure of $[Cu(bzsmp)_2Cl_2]$ with atomic numbering scheme. Color code: C, grey; H, orange; N, blue; O, red; S, purple; Cl, green; Cu, cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Crystal refinement parameters of $[Cu(bzsmp)_2Cl_2]$ (**2**).

Parameters	$[Cu(bzsmp)_2Cl_2]$
Color	Green
Crystal size (mm)	0.24 × 0.21 × 0.18
Empirical formula	$C_{32}H_{30}N_4CuO_4S_2Cl_2$
Formula weight	733.19
Space group	*P*21/*n*
Crystal system	monoclinic
T (K)	273(2)
λ (Mo Kα)	0.71073
a (Å)	13.0027(17)
b (Å)	8.2990(12)
c (Å)	15.634(2)
α (°)	90
β (°)	93.496(9)
γ (°)	90
V (Å^3)	1683.9(4)
Z	16
ρ_{calc} (Mg/m^3)	1.442
M (mm^{-1})	0.973
F(000)	1344
θ Range for data collection	1.98–40.01
Index ranges	$-22 \leqslant h \leqslant 23$, $-13 \leqslant k \leqslant 15$, $-24 \leqslant l \leqslant 28$
Reflections collected	38153
Independent reflections	10340
Data/restraints/parameters	10340/0/206
Goodness-of-fit on F^2	0.817
R_1, wR_2	0.0353, 0.1017
R_1, wR_2, (all data)	0.0736, 0.1367
Largest difference in peak and hole (e Å^{-3})	0.533 and −0.714

slow evaporation of the solvent the resulting complex **2** crystallized. Crystals of complex **2** were obtained after three weeks in 64% yield. Complex **2** has been structurally characterized by single crystal X-ray. The molecular structure of **2** is shown in Fig. 1. The physical and analytical data of compound **2** supports the X-ray structure.

4.1. IR spectra

A comparative study of the IR spectral data of the complex with ligand **1** gives meaningful information regarding bonding sites and its cyclization during complexation. The IR spectrum of **1** shows bands at 3252, 2969, 1658, 1071, 1598 and 877 which correspond to ν(NH), $\delta(CH_2)$, ν(CO), ν(N–N), ν(C=N) and ν(C–S), respectively [30]. The bands due to ν(NH) and ν(CO) are absent in **2** and a new band appears at 1254 cm^{-1} due to ν(C–O–C) which suggests cyclization [28,29] of acyclic {–C(O)–NH–N=C=} moiety by elimination of $HSCH_2C_6H_4$ during complexation with Cu(II). Thus I.R. data of **2** supports cyclization of **1** and formation of 1,3,4-oxadiazole moiety in the complex. A positive shift of 62 cm^{-1} in ν(N–N) as compared to the ligand suggests the involvement of this group as a bonding site.

Table 2
Selected bond lengths for the complex $[Cu(bzsmp)_2Cl_2]$ (Å) and angles (°).

Copper coordination sphere			
Bond length			
Cu(1)–N(1)	1.9999(10)	Cu(1)–O(1)	2.5080(4)
Cu(1)–Cl(1)	2.2830(4)	C(4)–C(19)	1.4532(18)
O(1)–C(3)	1.3612(16)	N(1)–C(19)	1.3013(15)
C(3)–C(4)	1.4018(18)		
Angles			
O(1)–C(3)–C(4)	116.41(12)	C(19)–N(1)–Cu(1)	132.65(8)
N(1)–C(19)–C(4)	131.88(10)	C(3)–C(4)–C(19)	121.30(11)
C(3)–O(1)–Cu(1)	124.18(12)		
Oxadiazole ring			
Bond lengths			
O(1)–C(18)	1.4280(17)	O(2)–C(15)	1.3607(17)
N(1)–N(2)	1.3986(14)	O(2)–C(19)	1.3631(14)
N(1)–C(19)	1.3013(15)	N(2)–C(15)	1.2929(15)
S(1)–C(15)	1.7268(12)	S(1)–C(17)	1.8285(17)
Angles			
N(2)–C(15)–S(1)	129.42(11)	C(7)–C(17)–S(1)	114.95(11)
C(15)–S(1)–C(17)	99.99(7)	O(2)–C(15)–S(1)	117.10(9)
N(1)–Cu(1)–N(1)#1	180.00(6)	N(1)–Cu(1)–Cl(1)#1	89.31(3)
Cl(1)–Cu(1)–Cl(1)#1	180.00(12)	N(1)#1–Cu(1)–Cl(1)#1	90.69(3)
		N(1)#1–Cu(1)–Cl(1)	89.31(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+1$, $-z+1$.

Table 3
Hydrogen bonds for $Cu(bzsmp)_2Cl_2$ (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
C(6)–H(6)···S(1)	0.93	2.970(3)	3.766(3)	144.57
C(17)–H(17A)···Cl(1)	0.97	2.900(12)	3.710(12)	141.70

4.2. UV spectra

The electronic spectrum of the ligand N^2-Hbmbh shows bands at 337, 252 and 213 nm assigned to the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. The magnetic moment of 1.82 B.M. for **2** is normal as expected for the presence of one unpaired electron. The complex $[Cu(bzsmp)_2Cl_2]$ displays electronic bands at 557, 316, 297, 257 nm. A Cu(II) complex with d^9 configuration is expected to experience Jahn–Teller distortion which leads to further splitting of the ^2Eg and $^2T_{2g}$ levels and give rise to the $^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), $^2B_{2g}$(ν_2), ^2E_g (ν_3) transitions which is expected to be close in energy and generally appear as a broad band. Therefore the broad band at 557 nm is assigned to the envelope of $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and ^2E_g transitions [38]. The strong absorptions found for complex **2** in the range 316–257 nm is due to the ligand to copper(II) charge transfer and intraligand transitions.

4.3. Crystal structure of complex 2

The crystal structure refinement data related to complex **2** are given in Table 1 and the main bond distances and bond angles of **2** are given in the Table 2. The hydrogen bonds are listed in Table 3. In the centrosymmetric mononuclear $[Cu(bzsmp)_2Cl_2]$, each Cu(II) ion is located at the inversion center. The six membered [CuO1C3C4C19N1] chelate ring is not coplanar (rms deviation from mean plane = 0.207 Å) but the two six membered chelate rings are parallel to each other separating a distance of 0.532 Å. Two ligands coordinate to Cu(II) center in meridonial fashion i.e. the carbonyl oxygen and hydrazinic nitrogen are cis to each. The bite angle for both C_3NCuO chelate rings is 75.28°. Cu(II) is bonded octahedrally with two methoxy oxygens, two oxadiazole nitrogens and two chlorine atoms with Cu–N, Cu–O and Cu–Cl distances of 1.9999(10) Å, 2.5080(4) Å, 2.2830(4) Å}, respectively (Fig. 1). Thus the ligand behaves as a neutral bidentate chelating ligand (Scheme 1). The Cu–N bond length in complex **2** agrees well with those

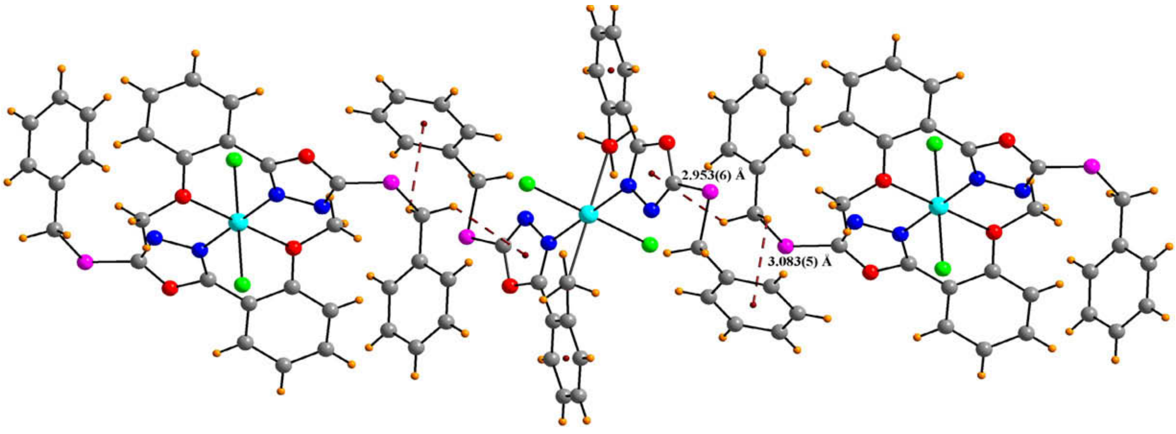


Fig. 2. One dimensional chain formed by C–H···π interaction (brown dotted) in the complex. Color code: C, grey; H, orange; N, blue; O, red; S, purple; Cl, green; Cu, cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

found for compounds e.g. [Cu(2-PBZM)MoO$_4$] {2-PBZM = 2-(2-pyridyl)benzimidazole) [39] and [Cu$_2$(EGTA)(Him)$_2$]$_n$, [Cu$_2$(EGTA)(Him)$_4$] · 4H$_2$O {Him = imidazole, EGTA = ethylenebis(oxyethylnitrilo)tetraaceticacid)}. The Cu–O bond length is comparably shorter than the sum of van der Waal's radii of oxygen and copper atoms (1.50 + 1.40 = 2.90 Å), indicating comparatively strong Cu–O bonding [40]. The 2-methoxybenzene and oxadiazole rings make a dihedral angle of 23.57°. Similarly, the dihedral angle between benzyl and oxadiazole rings is 57.46°. The plane containing the oxadiazole ring equally divides the 2-methoxy benzene ring in equal halves. The crystal packing of **2** reveals the existence of C–H···π, C–H···S and C–H···Cl intermolecular interactions. There are two C–H···π interactions, one occurring between a hydrogen atom of the methylene group and the π-electrons of the oxadiazole ring and the second one between other hydrogen of the same methylene group and the π-electrons of benzyl group from the adjacent molecule with a distance of 2.953(6) and 3.083(5) Å, respectively. These two C–H···π interactions provide one dimensional chain (Fig. 2). Additionally, two molecules of the complex are also linked by C–H···S interaction (2.970(3) Å) formed between C–H of 2-methoxy phenyl

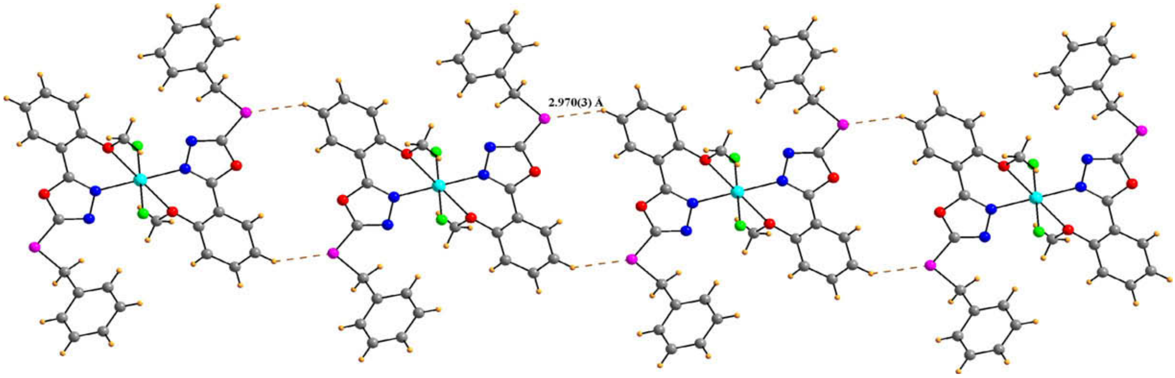


Fig. 3. One dimensional chain formed by C–H···S interaction (orange dotted) in complex. Color code: C, grey; H, orange; N, blue; O, red; S, purple; Cl, green; Cu, cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

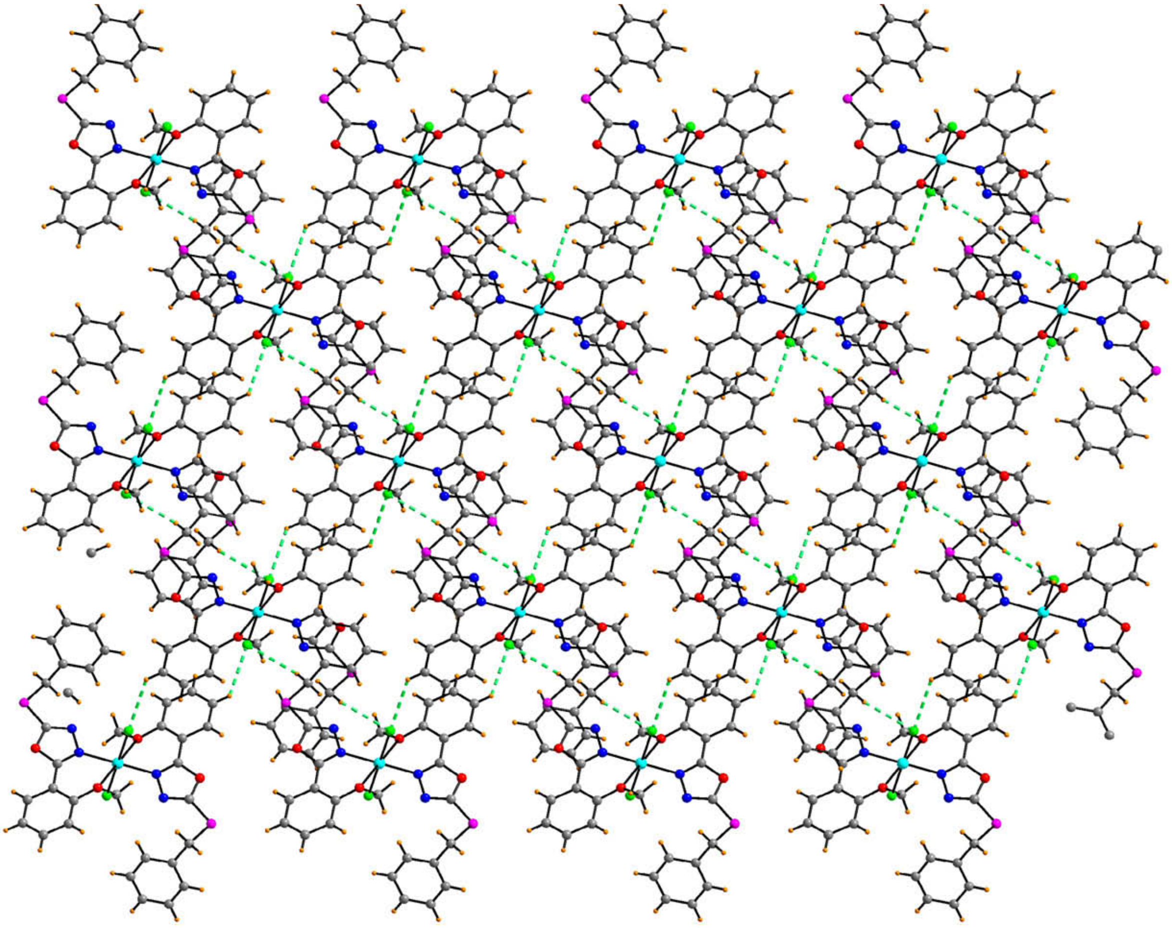


Fig. 4. Three-dimensional packing of complex [Cu(bzsmp)$_2$Cl$_2$] showing C–H···Cl interactions (green dotted). Color code: C, grey; H, orange; N, blue; O, red; S, purple; Cl, green; Cu, cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ring and sulfur atom which extend in one dimensional chain (Fig. 3). The three dimensional packing in the complex is also stabilized by two types of C–H···Cl interactions (one between hydrogen atom of methoxy phenyl ring and chlorine atom and other between hydrogen atom of benzyl ring and chlorine atom) with a distances of 2.951(6) and 2.900(12) Å, respectively (Fig. 4).

5. Conclusion

We have reported that acyldithocarbazates derivatives undergo cyclization during complex formation in the presence of en [13]. The present work indicates that the presence of Cu(II) is required for the cleavage of C–S bond leading to the elimination of $C_6H_5CH_2SH$ and cyclization of the cleaved product. As a conclusion of this work we describe a very facile route to obtain 2-benzylsulfanyl-1,3,4-oxadiazole as a stable Cu(II) complex.

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Appendix A. Supplementary data

CCDC 685385 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.10.016.

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