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Synthesis, spectroscopic and crystal structure investigation of $[Cu(bzsmp)_2Cl_2]$; {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

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ABSTRACT

The ligand N^2-[bis(benzylsulfanyl)methylene]-2-methoxybenzohydrazide (N^2-bmbh) (**1**) on reaction with $CuCl_2.2H_2O$ yielded the mononuclear complex $[Cu(bzsmp)_2Cl_2]$ (**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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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; $\nu(CH_2)$ 2979; ν(Cu–N) 478, ν(Cu–O) 420, ν(Cu–Cl) 325.

2.4. Physical measurements

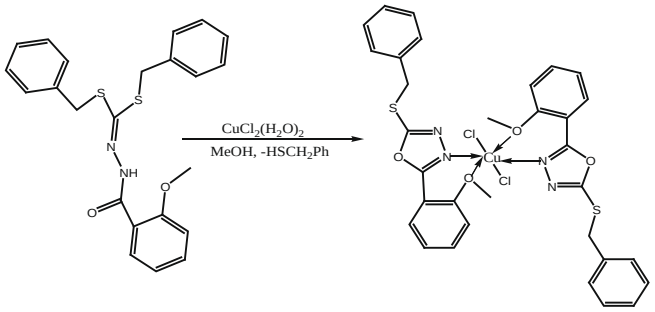
Carbon, hydrogen and nitrogen contents were estimated on a CHN Analyser Model CE-440. Magnetic susceptibility measurement was performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant and electronic spectra were recorded on UV-1700 Pharmaspec spectrophotometer. IR 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 $[Cu(bzsmp)_2Cl_2]$.

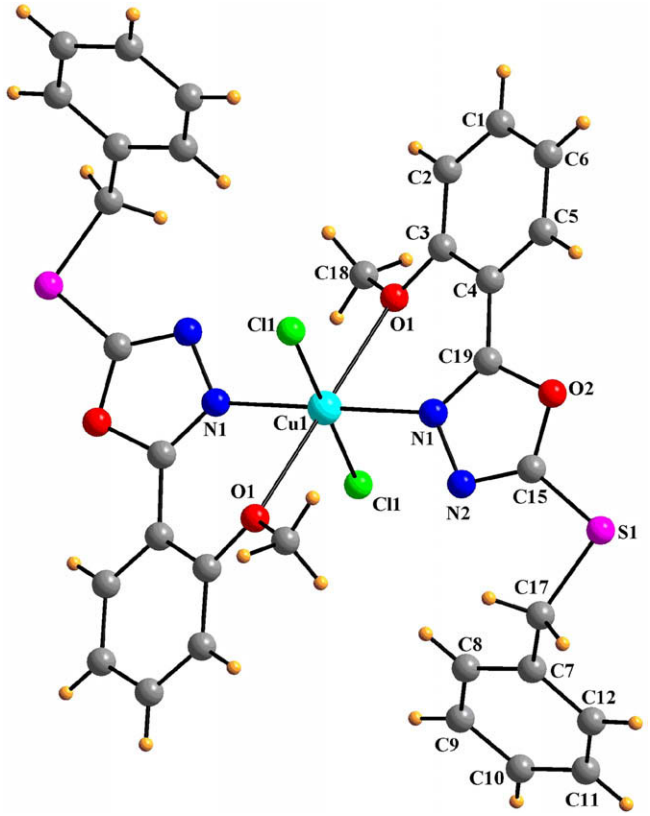


Fig. 1. Molecular structure of $[Cu(bzsmp)_2Cl_2]$ with atomic numbering scheme. Color code: C, grey; H, orange; N, blue; O, red; S, purple; Cl, green; Cu, cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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	$P21/n$
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	38 153
Independent reflections	10 340
Data/restraints/parameters	10 340/0/206
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