Synthesis and Spectroscopic Characterization of the Benzaldehyde Schiff Base of *S*-Allyldithiocarbazate and its Copper(II) Complex and the X-ray Crystal Structure of Bis[*S*-allyl-β-*N*-benzylidene)dithiocarbazato]Copper(II)

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Received October 15th, 2007; accepted November 19th, 2007.

Abstract. S-allyl- β -N-(benzylidene)dithiocarbazate (sabdtc, 1), prepared from hydrazine hydrate, carbon disulfide, allyl bromide and benzaldehyde, reacts with copper(II) nitrate in ethanol solution to form the complex Cu(sabdtc)₂ (2). 1 function as a single negatively charged bidentate chelating ligand and coordinates via the azomethine nitrogen atom and thioenolate sulfur atom to the metal ion. 1 and 2 were characterized by elemental analyses, ¹H NMR, ¹³C NMR, UV/Vis, IR, and mass spectra. Spectroscopic evidences suggest a four-coordinate distorted square planar structure for **2**. The molecular and crystal structure of **2** was determined by single crystal X-ray analysis. Crystallographic data for **2** at 291(2) K: space group C2/c, a = 20.340(3), b = 15.503(3), c = 7.659(1) Å, $\beta = 95.96(2)^{\circ}$, Z = 4, $R_1 = 0.044$ and wR2 = 0.0689.

Keywords: Copper; S-allyldithiocarbazate; Crystal structures; Bidentate NS Schiff base

1 Introduction

Dithiocarbazates constitute an important class of mixed hard-soft nitrogen-sulfur donor ligands [1, 2]. There is continuing interest in the coordination chemistry of heterocyclic bidentate ligands containing the NS donor set [3]. Copper complexes of dithiocarbazates have been of interest in numerous studies because of their chemical and biological properties [4–7].

The dithiocarbazate Schiff base compounds RCH= NNHC(S)SR' are known to coordinate via extended π -conjugation through ligand deprotonation [8] and give corresponding copper(II) ion complexes that have attracted considerable interest because of the occurrence of the CuN₂S₂ chromophore in blue copper proteins such as plastocyanin [9].

The allyl group in the molecule structure has inclined for many interesting chemical reactions and can be used as a ligand [10–12]. Although, most previous studies on dithiocarbazates were based on S-methyl and S-benzyl dithiocarbazate chelating agents, Schiff base ligands derived from S-allyldithiocarbazates have not received much attention.

Herein, we describe the synthesis, characterization and crystal structure of bis[S-allyl- β -N-(benzylidene)dithiocar-bazato]-copper(II) complex.

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2 Experimental Section

2.1 Materials and physical measurements

All materials were purchased form Merck Chemical Company and were used as received. All solvents were reagent grade and used without further purification. C, H, N, S elemental analyses were performed using a Thermo Finnigan Flash 1112EA elemental analyzer. The IR spectra were recorded using a Buck 500 Scientific spectrometer in the range 4000-400 cm⁻¹ and far-IR on a Thermo Nicolet NEXUS 870 FT-IR in the range 700-200 cm⁻¹ as KBr pellets. The mass spectra were recorded on a Varian CH-7 instrument at 70 eV.

The ¹H and ¹³C NMR measurements were performed on a Bruker BRX 500 AVANCE 500 MHz spectrometer. Samples were dissolved in DMSO-d₆ with TMS as internal reference. Melting points (m.p.) were determined by DSC technique.

2.2 Preparation of S-allyl-β-N-(benzylidene)dithiocarbazate (sabdtc, 1)

To a mixture of 5 ml (0.1 mol) hydrazine hydrate and 5.6 g (0.1 mol) KOH in 30 ml of ethanol at 5 °C, was added a solution of 6.1 ml (0.1 mol) of carbon disulfide and 8.6 ml (0.1 mol) of allyl bromide with continuous string. To this mixture was added the ethanolic solution (25 ml) of benzaldehyde (11.1 ml, 0.1 mol) and heated. The yellow product was separated by filtration, washed with water and dried in a vacuum. 1 was recrystallized from ethanol. Yield 49.5% (based on benzaldehyde); m.p. 137 °C. $C_{11}H_{12}N_2S_2$ (236.36), Anal. calc.: C, 55.90; H, 5.12; N, 11.85; S, 27.13 for C H N S Found: C, 55.96; H, 5.00; N, 11.85; S, 28.26%. Mass spectrometry: m/z = 236, 163, 118, 104, 90, 77, 41 and 28.

¹**H** NMR (500 MHz, DMSO-d₆, 25 °C): δ = 3.90 (d, 2H; C2), 5.24 (dd, 2H; C4), 5.87-5.96 (m, H; C3), 7.45 (dd, 3H; C7, C9, C11), 7.71 (dd, H; C8,



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C10), 8.24 (s, H; C5), 13.34 (s, H; NH). ¹³C NMR (500 MHz, DMSO-d₆, 25 °C): δ = 196.44 (C1), 146.56 (C5), 133.28 (C6), 133.16 (C9), 130.77 (C3), 128.95 (C7, C11), 127.42 (C8, C10), 118.45 (C4), 35.98 (C2).

2.3 Preparation of bis[S-allyl-β-N-(benzylidene)dithiocarbazato]-copper(II) complex (Cu(sabdtc)₂, 2)

Copper(II) nitrate trihydrate (0.242 g; 0.001 mol) in ethanol (10 ml) was added to the ethanolic solution of 1 (0.473 g; 0.002 mol). The mixture was heated and then left to stand overnight. The product was filtered off, washed with ethanol, dried in a vacuum. Yield 68.97 % (based on 1); m.p. 125 °C. $C_{22}H_{22}CuN_4S_4$ (534.24), Anal. Found: C, 49.46; H, 4.15; N, 10.49; S, 24.01; Cu, 11.51. Calc: C, 49.38; H, 4.04; N, 10.39; S, 24.88; Cu, 11.89 %. Mass spectrometry: m/z = 534, 236, 162, 104, 90, 77, 41 and 28.

2.4 Crystal structure determination of 2

Well shaped crystals of the compound investigated at 18 °C on an STOE IPDS, using graphite monochromatized Mo-Kα radiation($\lambda = 0.71073$ Å). Crystal data, as well as details of data collection and structure refinement are listed in Table 1. For all data LP corrections were applied. The structure was solved by direct methods [13] and subsequent Fourier-syntheses. Approximate positions of all hydrogen atoms with the exception of the ones within the disordered part of the ligand were found via difference Fouriersyntheses. Taking into account the disorder of the allyl group (occupation 0.50(2):0.50(2)), has been refined by full-matrix leastsquares calculations on F^2 [14] (applying appropriate distance and displacement parameter restraints and constraints for the disordered region) converged (max. shift/esd: 0.000) to the final indicators given in Table 1. Refined parameters include anisotropic displacement parameters for all the non-hydrogen atoms. The H atoms were treated as riding on their parent carbon atoms in idealised positions. Isotropic displacement parameters were kept equal

Table 1 Crystal data, and structure refinement for Cu(sabdtc)₂

	a a a	
Empirical formula	$C_{22}H_{22}CuN_4 S_4$	
Formula weight	534.27	
Temperature	291(2) K	
Wavelength	0.71073 A	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 20.340(3) Å	$\alpha = 90^{\circ}$
	$b = 15.503(3) \text{ Å}_{a}$	$\beta = 95.956(17)^{\circ}$
	c = 7.6549(11) Å	$\gamma = 90^{\circ}$
Volume	2400.8(7) Å ³	
Ζ	4	
Density (calculated)	1.478 g/cm ³	
Absorption coefficient	1.275 mm^{-1}	
F(000)	1100	
Crystal size	$0.10 \times 0.05 \times 0.03 \text{ mm}$	
Theta range for data collection	2.01 to 26.06°	
Index ranges	$-25 \le h \le 25, -18 \le k \le 19$, −9≤ <i>l</i> ≤9
Reflections collected	13258	
Independent reflections	2369 $[R_{(int)} = 0.0909]$	
Completeness to $\theta = 26.06^{\circ}$	99.5 %	
Absorption correction	none	
Refinement method	Full-matrix least-squares	on F^2
Data / restraints / parameters	2369 / 61 / 164	
Goodness-of-fit on F^2	0.942	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0442, wR2 = 0.0$	689
R indices (all data)	$R_1 = 0.1402, wR2 = 0.0$	756
Largest diff. peak and hole	0.291 and $-0.262 \text{ e.}\text{Å}^{-3}$	
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to 120 % of the equivalent isotropic displacement parameters of the parent carbon atom. Scattering factors, dispersion corrections and absorption coefficients were taken from International Tables for Crystallography (1992, Vol. C, Tables 6.114, 4.268 and 4.2.4.2).

3 Results and Discussion

3.1 Spectroscopic characterization

In recent years, the interesting complexes of *S*-methyl and *S*-benzyl dithiocarbazate have been prepared but *S*-allyldithiocarbazate is a new series of this kind of compounds.

The S-allyl- β -N-(benzylidene)dithiocarbazate (sabdtc) has the thioamide function -N(H)C(S) in order to be occurred complexation. As be shown in Figure 1 the free ligand must exhibit thiol-thione tautomers.



Figure 1 Tautomeric forms of thione and thiol of free ligand (sabdte, 1)

In the present of transition metal ions, the Schiff base compound is converted into the thiol tautomeric form to facilitate the formation of centric neutral bis-ligand metal complexes [15]. The thiolo sulfur and azomethine nitrogen like as the other kinds of these complexes coordinate to metal atoms. However their IR spectra (Table 2) do not show any band at ca. 2750 cm⁻¹ that may be assigned to v(S-H), and it exhibits v(N-H) at ca. 3104.9 cm⁻¹ as a medium band. According to the above mentioned data, one may conclude that in solid state, the thione form must be predominated. The v(N-H) bond in free ligand disappear in complex spectra that indicate deprotonation of ligand during the complexation occur. In comparing the IR spectra of starting ligand with synthesized complex, we find that the vibrational band of v(C=N) has been red shifted from 1609.8 cm^{-1} to 1592.8 cm^{-1} . The two bands at 676 and 673 cm⁻¹ in Schiff base and Cu^{II} complex, respectively, has been assigned to out of plain vibrations of mono substituted aromatic ring. The C=C bond of allyl group has been located at 1636.3-1631.6 cm⁻¹. The IR spectrum in region 700-200 cm⁻¹ show two bands at 352 and 478 cm⁻¹ attributed to S-Cu and N-Cu, respectively.

The main parameters of ¹H NMR and ¹³C NMR spectra in DMSO are collected in Section 2.2. The ¹H NMR of free ligand **1** showed a peak at ca. 13.34 ppm attributed to the resonance of NH proton, that disappear this peak in deuteration, indicating that the ligand has lost a proton on deuteration. The signal of the proton on C=N double bond

	IR bands (cm ⁻¹) ^a							
compound	NH	C=C	C=N	C=S	N-N	M-N	M-S	Electronic spectra (in CH_2Cl_2) $\lambda max (log \epsilon)^{b}$
sabdtc	3104.9	1636.3	1609	1097	1025.4	_	_	240(3.98), 334(4.56)
Cu(sabdtc) ₂	-	1631.6	1592.8	_	1024.3	478	352	252(4.70), 317(4.86), 366(4.84), 439(3.71)

Table 2 Main IR spectral vibrations (cm⁻¹) and electronic spectral data

^{a)} wavenumbers are in units cm⁻¹ ^{b)} Units of λ_{max} are in nm and loge (dm³ mol⁻¹cm⁻¹) are given in parentheses.

appears at 8.24 ppm. The resonance peaks associated with the aromatic groups are observed in the range 7.45–7.71 ppm. However, its ¹H NMR spectrum does not display any signal at approximately 4.00 ppm that is related to the S–H proton, indicating in DMSO solution it exists as the thione tautomer [16]. The protons of SCH₂, CH and CH₂ moieties display doublets, doublet of doublet and a multiple at 3.90, 5.14 and 5.87-5.96 ppm, respectively.

The ¹³C NMR spectrum of **1** showed a signal at low field 196.44 ppm corresponding to the thioamide carbon is found in DMSO at room temperature. In addition, the azomethine carbon signal of ligand appears at 146.56 ppm. The SCH₂, CH and CH₂ carbon atoms in allyl group show signals at 35.98, 130.77 and 118.45 ppm, respectively. The signals of the carbon atoms on phenyl ring appear at 127.42 to 133.28 ppm.

The Schiff base mass spectra show parent ions peaks at m/e 236 and the main fragmentation includes the loss of phenyl with ion peak at m/e 77; the other peaks at m/e 163, 118, 104, 90, 41 and 28 corresponds to $[PhCH=NN(H)C(S)]^+$, $[PhCH=NN(H)C]^{3+}$, $[PhCH=N]^+$, $[PhCH]^{2+}$, allyl⁺ and N₂, respectively. The molecular ion for Cu^{II} complex is detected at m/e 534. The fragments m/e 236, 162, 104, 90, 77, 41 and 28 attributed to sabdtc, $[PhCH=NN(H)C(S)]^+$, $[PhCH=N]^+$, $[PhCH]^{2+}$, Ph, allyl⁺, N₂, respectively.

The electronic spectra in range of 200 to 380 nm in CH₂Cl₂ solution are characteristic of L-L* absorption. The absorption maxima at 252, 317 and 366 nm can be attributed to intra-ligand transitions only. The $\pi \rightarrow \pi^*$ band transition, of the ligand is observed at 366 nm that is red shifted by ca. 30 nm metal complex. This bathochromic shift can be attributed to overlap of the Cu-d-orbital with the p-orbital of the donor atom, which causes an increase in conjugation in the ligand and thus lowers the $\pi \rightarrow \pi^*$ energy. The absorption peak at 240 nm is assigned to phenyl ring in ligand that shows a hypsochromic shift by ca. 14 nm in the complex. The band appearing at 366 nm in the complex bearing deprotonated ligand may have resulted from the extended conjugation in the ligand forced by the chelated metal ion [17]. The presence of chalcogen donor atoms in the ligands brings about strong CT band at 439 nm in the complex. The tail of CT band extend up to the visible portion of the spectrum with this result that no d-d bands are generally observed in the electronic spectra of such complex [18].



Figure 2 ORTEP diagram of $Cu(sabdtc)_2$ showing the atom labelling scheme; displacement ellipsoids are drawn at the 30 % probability level; symmetry code: A -x, -y, -z. Note the one to one disorder of the *S*-allyl groups.

3.2 X-ray crystal structure of 2

Crystal data, as well as details of data collection and structure refinement are compiled in Table 1. An ORTEP diagram of the bis[*S*-allyl- β -*N*-(benzylidene)dithiocarbazato]copper(II) molecule (**2**), with the atom numbering scheme is shown in Figure 2 and the stacking of the molecules in the crystal is illustrated in Figure 3. it should be pointed out that titled complex crystallographically imposed inversion symmetry.

The Schiff base is coordinated to the Cu^{II} ion in its deprotonated iminothiolate form. This form results in delocalization of the negative charge caused by the deprotonation of the NH proton as indicated by the intermediate C5-N1, N1-N2, N2-C1 bands.

Two ligands coordinate to the Cu^{II} atom to form two five-membered chelate rings Cu1-N1-N2-C1-S1. The coordination of copper(II) is monomeric and distorted squareplanar with two equivalent Cu-N (1.995(4) Å) and Cu-S (2.254(1) Å) bonds. The coordinated mercapto sulfur and methine nitrogen atoms in the two ligands are in opposite positions so that the complex has trans-configuration allyl group moieties on the opposite side and thio S and imine nitrogen atoms are cis to each other [19]. The bond distances C(1)-N(2), 1.290(5) Å and C(1)-S(1), 1.692(5) Å suggest a C=N double bond and C-S single bond [8]. One intersting feature of our complex is the present of two equal C=N bonds (N2-C1, N1-C5). The copper(II)-donor atom distances, namely Cu-S [2.254(1) Å], Cu-N [1.995(4) Å]



Figure 3 Stacking of the molecules along the *c*-axis of the unit cell. Note the secondary Cu···S interactions between neighbouring molecules. Symmetry codes: A -x, -y, -z; B x, -y, -0.5+z; C -x, y, -0.5-z; D x, -y, -1.5+z; E -x, -y, -1-z; F x, -y, -2.5+z; G -x, y, -1.5-z.

Table 3 Selected bond lengths/Å and bond angles/° for Cu(sabdtc)₂

Cu(1)-S(1)	2.254(1)	S(1)-Cu(1)-N(1)	84.1(1)
Cu(1)-N(1)	1.995(4)	S(1)-Cu(1)-N(1)A	95.9 (1)
S(1)-C(1)	1.692(5)	Cu(1)-S(1)-C(1)	95.2(2)
S(2)-C(1)	1.731(5)	C(1)-S(2)-C(21)	102.8(8)
S(2)-C(21)	1.799(1)	C(1)-S(2)-C(22)	105.1(8)
S(2)-C(22)	1.796(1)	Cu(1)-N(1)-N(2)	119.6(3)
N(1)-N(2)	1.397(5)	Cu(1)-N(1)-C(5)	124.6(4)
N(1)-C(5)	1.290(6)	N(2)-N(1)-C(5)	115.6(4)
N(2)-C(1)	1.290(5)	N(1)-N(2)-C(1)	112.6(4)
C(21)-C(31)	1.494(1)	S(1)-C(1)-S(2)	114.6(3)
C(31)-C(41)	1.304(1)	S(1)-C(1)-N(2)	127.3(4)
C(22)-C(32)	1.492(1)	S(2)-C(1)-N(2)	118.1(4)
C(32)-C(42)	1.306(1)	S(2)-C(21)-C(31)	109.7(1)
C(5)-C(6)	1.441(7)	S(2)-C(22)-C(32)	109.3(1)
C(6)-C(7)	1.342(6)	C(21)-C(31)-C(41)	123(2)
C(6)-C(11)	1.374(6)	C(22)-C(32)-C(42)	113(2)
C(7)-C(8)	1.367(7)	N(1)-C(5)-C(6)	132.2(5)
C(8)-C(9)	1.364(7)	C(5)-C(6)-C(7)	126.5(5)
C(9)-C(10)	1.331(6)	C(5)-C(6)-C(11)	116.3(5)
C(10)-C(11)	1.349(6)	C(7)-C(6)-C(11)	117.0(5)
		C(6)-C(7)-C(8)	121.1(5)
		C(7)-C(8)-C(9)	120.4(6)
		C(8)-C(9)-C(10)	118.8(6)
		C(9)-C(10)-C(11)	120.4(6)

Symmetry code: A -x, -y, -z

could be compared well with other related published work [8].

The dihedral angle between the phenyl ring and the fivemembered ring Cu1S1C1N2N1 is ca. 5°.

The coordination environment of copper(II) atom may be considered as distorted square planar. The S1-Cu-N1 and S1-Cu-N1A angles are 84.1(1)° and 95.9(1)°, which is shorter and larger than the expected ideal value of 90°, respectively. This distortion may be attributed to the restricted bite angles which to be imposed by the planar bidentate Schiff bases. For further information, the bond angles of this complex have reported in table 3.

4 Conclusion

The reaction of copper nitrate with the bidentate Schiff bases derived from *S*-allyldithiocarbazate and benzaldehyde in ethanol produces a new crystalline green complex. The X-ray crystal structure determination of $Cu(sabdtc)_2$ shows that it has a four NS coordinate distorted square planar geometry.

Supplementary material. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 663339 for compound **2**. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement. We thank Ms E. Hammes for support during the X-ray data collection.

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