Journal of Molecular Structure 936 (2009) 257–263

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Nickel(II) and copper(II) complexes of 5-(4-methoxy-phenyl) [1,3,4]-oxadiazole-2-thione: Synthesis and X-ray characterization

N.K. Singh [a,*], S.K. Kushawaha [a], M.K. Bharty [a], Ram Dulare [a], R.J. Butcher [b]

[a] Department of Chemistry, Banaras Hindu University, Varanas 221005, India
[b] Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA

ARTICLE INFO

Article history:
Received 26 June 2009
Received in revised form 2 August 2009
Accepted 6 August 2009
Available online 11 August 2009

Keywords:
5-(4-Methoxy-phenyl) [1,3,4]-oxadiazole-2-thione
Mixed ligand complexes
X-ray structure
Supramolecular architecture

ABSTRACT

Two new mixed ligand complexes $[Ni(en)_2(mot)_2]$ (**1**) and $[Cu(en)_2(mot)_2]$ (**2**) derived from potassium *N'*-(4-methoxy-benzoyl) dithiocarbazate $[K^+(H_2L)^-]$ containing en as the coligand have been synthesized. $[K^+(H_2L)^-]$ undergoes cyclization in the presence of ethylenediamine and is converted to 5-(4-methoxy-phenyl [1,3,4]-oxadiazole-2-thione $(mot)^-$. $[Ni(en)_2(mot)_2]$ and $[Cu(en)_2(mot)_2]$ have been characterized by various physicochemical techniques and single crystal X-ray. In $[Ni(en)_2(mot)_2]$ and $[Cu(en)_2(mot)_2]$ the metal ion has MN_6 core with six coordinate octahedral arrangement from four N atoms of two en and two N atoms from two mot anions.

1. Introduction

N-aroyl dithiocarbazates and their salts can be converted to 1,3,4-oxadiazole-2-thiol/thione which exhibit relevant biological properties and have a wide variety of applications, in both medicine and agriculture [1]. Several methods have been used for the synthesis of these compounds from acyclic precursors. Some of them are oxidative cyclization of acyl hydrazone [2], acylthiourea [3–5] and acylthiosemicarbazide [6–9]. The heterocyclic thiones represent an important type of compounds in the field of coordination chemistry because of their potential multifunctional donor sites, i.e., either exocyclic or endocyclic nitrogen [10]. The cyclization of 3-acyldithiocarbazate esters, *N*-aroyl dithiocarbazates and their salts to the corresponding 1,3,4-oxadiazole in the presence of a base is reported in the literature [11–15]. It is known that the salts of *N*-aroyl dithiocarbazates can be converted to 1,3,4-oxadiazole-2-thiol in the presence of a base [13], it was thought whether the *N*-aroyl dithiocarbazate bonded to a transition metal can be converted to 1,3,4-oxadiazole-2-thione. Accordingly the Cu(II) complex of 4-methoxy-benzoyl dithiocarbazate was reacted with an excess of ethylenediamine and the results of this investigation is presented here.

2. Results and discussion

A methanol solution of $[Ni(en)_2(NCS)_2]$ on reaction with $[K^+(H_2L)^-]$ yields $[Ni(en)_2(mot)_2]$ (**1**). The reaction of $[K^+(H_2L)^-]$ with $CuCl_2{\cdot}2H_2O$ gave a blue precipitate which dissolved in methanolic solution of en on heating at 60 °C to form $[Cu(en)_2(mot)_2]$ (**2**). A simple scheme showing the syntheses of $[K^+(H_2L)^-]$ and the complexes **1** and **2** are given below.

The complexes are air stable, non-hygroscopic shiny crystalline solids, which are insoluble in common organic solvents but soluble in dimethyl formamide (DMF) and dimethylsulfoxide (DMSO). The complexes were fully characterized by magnetic susceptibility measurements, IR, UV–vis and X-ray spectroscopies. Analytical data of the complexes (recorded in Section 4) corroborated well with their respective formulations. ^1H NMR spectrum of $[K^+(H_2L)^-]$ in DMSO-d_6 shows signals at δ 9.65 (2H, NH) and 3.50 (3H, $-OCH_3$) ppm. The benzene ring protons appear as multiplet between 7.0 and 7.7 ppm (m, 4H). The ^{13}C NMR spectrum of $[K^+(H_2L)^-]$ shows signals at δ 178.90, 160.38 and 55.28 ppm which are due to the C=S, C=O and OCH_3 carbons, respectively. The IR spectrum of $[K^+(H_2L)^-]$ in KBr is expected to give rise to characteristic bands due to ν(NH), ν(C=O), ν(N—N) and ν(C=S) which occur at 3246 and 3169; 1637, 1000 and 886 cm^{-1}, respectively. The absorptions appearing in the region 3244–3122 cm^{-1} due to NH stretching vibrations of en are shifted to lower frequency than those encountered in the free en [16]. A negative shift in $\nu(NH_2)$ of en and appearance of a new band due to M—N near 468–471 cm^{-1} suggest formation of a chelate. The IR spectra of the

---

[*] Corresponding author. Address: Department of Chemistry, Banaras Hindu University, Varanas 221005, Uttar Pradesh, India. Tel.: +915426702452; fax: +915422368127.
E-mail address: singhnk_bhu@yahoo.com (N.K. Singh).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.08.006

complexes are devoid of any peak due to ν(NH) (hydrazinic) (3246 cm^{-1}) which was present in the precursor [Cu(HL)$_2$]. Additionally, ν(C=O) (1637 cm^{-1}) disappeared and new peaks appeared due to the endocyclic C=N and C—O—C at 1608–1585 and 1255–1226 cm^{-1}, respectively, suggesting cyclization of the dithiocarbazate moiety. The IR data are thus consistent with the formation of 1,3,4-oxadiazole moiety during complexation [17]. The magnetic moment and electronic spectral data were used to determine the geometry of the complexes. [Ni(en)$_2$(mot)$_2$] exhibits a magnetic moment of 2.86 B.M. and shows a band at 17,860 cm^{-1} which is considered to arise from the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$ transition in an octahedral geometry around Ni(II) [18]. [Cu(en)$_2$(mot)$_2$] shows a magnetic moment of 2.01 B.M. and a broad band at 16400 cm^{-1} assigned to the $^2T_{2g} \rightarrow {}^2E_g$ transition for an octahedral geometry around Cu(II) [18].

Molecular structures of **1** and **2** were determined crystallographically. The details of data collection, structure solution and refinement are listed in Table 1. The Ortep diagram of complex **1** and molecular structure of the complex **2** with atom numbering scheme are shown in Figs. 1 and 5, respectively. The selected bond lengths and angles are given in Tables 2 and 3. The single crystal X-ray diffraction studies indicate that the ligand (mot$^-$) adopts the thione form in **1** and **2**. The X-ray structure of complex **1** shows the presence of two independent complexes in the asymmetric unit and in each unit the Ni atom is on a center of inversion. The X-ray crystal structures of both units of **1** show the presence of two mot$^-$ as ligand coordinated to Ni(II) in a distorted octahedral geometry (Fig. 1) having axial bond angles of 90.52(7)° and 87.66(8)° but equatorial bond angles of 82.75(8)° and 82.96(8)°, respectively in units containing Ni(1) and Ni(2). The coordination environment is fulfilled by two axial (mot)$^-$ ions at the trans positions, bonded through oxadiazole nitrogen atoms at the distances

Table 1
Crystal data for (**1**) and (**2**).

	1	**2**
Empirical formula	$C_{22}H_{30}N_8NiO_4S_2$	$C_{22}H_{30}CuN_8O_4S_2$
Formula weight	593.37	598.20
T (K)	295(2)	295(2)
λ/Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*P*21/*n*
a (Å)	8.1852	9.6756(4)
b (Å)	13.404	12.2074(4)
c (Å)	13.954	11.5411
α (°)	111.63	90 0
β (°)	106.561	107.672(4)°
γ (°)	92.842	90 0
V (Å^3)	1343.5(5)	1298.83(8)
Z	2	2
D_{calc}/Mg m^{-3}	1.467	1.530
μ (mm^{-1})	0.922	1.047
Crystal size (mm)	0.53 × 0.41 × 0.34	0.57 × 0.39 × 0.35
Reflections collected	40498	24231
Independent reflections	9076 (R_{int} = 0.0423)	4428 (R_{int} = 0.0283)
Data/restrains/parameters	9076/0/337	4428/0/170
Goodness-of-fit	1.062	1.069
R factor [$I > 2\sigma(I)$]	0.0411	0.0291
wR_2 [$I > 2\sigma(I)$]	0.1053	0.0732
R factor (all data)	0.0851	0.0609
wR_2 (all data)	0.1387	0.0929
Largest diff. peak/hole (e Å^{-3})	0.826, −0.465	0.631, −0.241

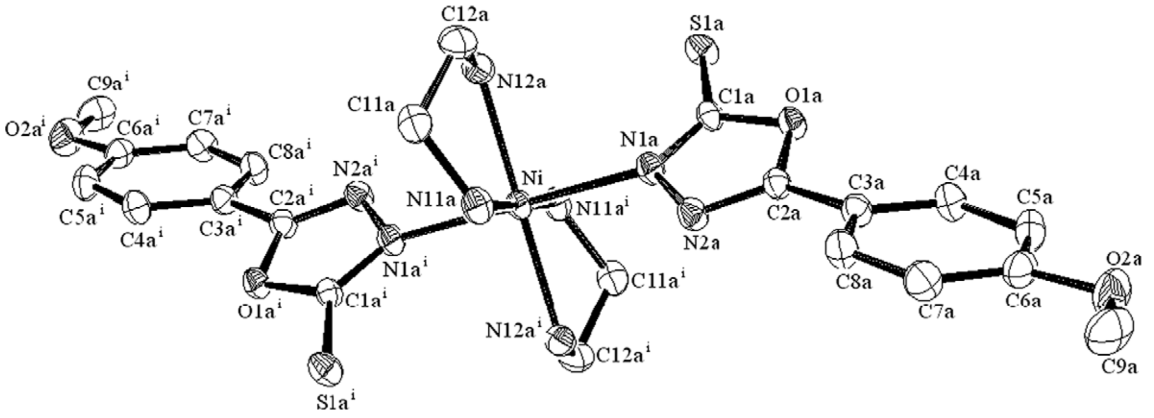

Fig. 1. Ortep plot of [Ni(en)$_2$(mot)$_2$] showing atomic numbering scheme with ellipsoid of 30% probability. Hydrogen atoms are omitted for clarity (symmetry code i = $-x$, $-y+1$, $-z+1$).

Table 2
Selected bond lengths (Å) and bond angles (°) for [Ni(en)$_2$(mot)$_2$].

Ni (**1**)		Ni (**2**)	
Ni(1)—N(12A)	2.144(2)	Ni(2)—N(12B)	2.092(18)
Ni(1)—N(1A)	2.107(17)	Ni(2)—N(1B)	2.156(2)
Ni(1)—N(11A)	2.084(18)	Ni(2)—N(11B)	2.102(2)
S(1A)—C(1A)	1.699(2)	S(1B)—C(1B)	1.685(2)
O(1A)—C(2A)	1.363(2)	O(1B)—C(2B)	1.366(3)
O(1A)—C(1A)	1.392(2)	O(1B)—C(1B)	1.399(3)
C(1A)—N(1A)	1.312(3)	C(1B)—N(1B)	1.320(3)
N(11A)#1—Ni(1)—N(1A)#1	89.33(7)	N(11B)#2—Ni(2)—N(1B)#2	90.59(9)
N(11A)—Ni(1)—N(1A)#1	90.67(7)	N(11B)—Ni(2)—N(1B)#2	89.41(9)
N(12A)#1—Ni(1)—N(1A)#1	90.52(7)	N(12B)#2—Ni(2)—N(1B)#2	87.66(8)
N(12A)—Ni(1)—N(1A)#1	89.48(7)	N(12B)—Ni(2)—N(1B)#2	92.34(8)
N(12A)#1—Ni(1)—N(11A)#1	82.75(8)	N(12B)#2—Ni(2)—N(11B)#2	82.96(8)
N(12A)—Ni(1)—N(11A)#1	97.25(8)	N(12B)—Ni(2)—N(11B)#2	97.04(8)

#1, $-x$, $-y+1$, $-z+1$; #2, $-x-1$, $-y+2$, $-z+1$.