

Crystal Structure and Spectroscopic Studies of Bis(morpholine dithiocarbamate) Nickel(II) Complex, $\text{Ni}(\text{C}_4\text{H}_8\text{ONCS}_2)_2$

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The title compound has been prepared and characterized by EA, IR and TG spectral studies. The crystal structure of nickel (II) bis(morpholine dithiocarbamate) $\text{Ni}(\text{C}_4\text{H}_8\text{ONCS}_2)_2$ is determined by X-ray diffraction methods. It crystallizes in the monoclinic system, space group $P2_1/n$, with lattice parameters $a = 0.4288(1)$, $b = 2.0526(4)$, $c = 0.8333(2)$ nm, $\beta = 97.43(3)^\circ$, and $Z = 2$. In the structure, central Ni atom coordination geometry is slightly distorted square-planar with the four S atoms from two morpholine dithiocarbamate ligands. The four Ni—S bond distances are in the range of 0.2199(5)—0.2201(2) nm. The IR spectral data are in agreement with the structural ones. The TG data indicate that it decomposed completely at the 766.89°C.

Keywords Crystal structure, morpholine, nickel complex, slightly distorted square-planar

Introduction

Substituted dithiocarbamate anions have proved to be highly versatile chelating agents for the separation of metals as metal chelates by gas chromatography.¹ Some of substituted dithiocarbamate salts have also shown interesting biological effects which include anti-alkylation or anti-HIV properties.^{2,3} The ability of dithiocarbamate to bind to metal has been known for many years. It forms a chelate with virtually all transition elements.⁴ Morpholine dithiocarbamate has been suggested as a possible analytical reagent in the spectrophotometric and volumetric determination of some 34 metal elements.⁵ It has been utilized in the gravimetric determination of tellurium, copper, bismuth, palladium and nickel.⁶ The reagent was used in the thin layer and paper chromatographic separation of metal complexes.⁷ The reagent has

been applied to determination of metals in biological fluids, *e. g.* enzymes, beef liver and beef pancreas, also in alloys.¹ In this paper, we report the crystal structure of the title compound. Also IR and TG spectra of the title compound have been determined.

Experimental

Synthesis

All chemicals were obtained from a commercial source and used without further purification.

Preparation of the compound $\text{C}_4\text{H}_8\text{ONCS}_2\text{Na}$

To a stirred solution of morpholine (1.00 g, 11.5 mmol) in CH_3CN (100 mL) was added, at less than 4°C, carbon disulfide (0.874 g, 11.5 mmol) and sodium hydroxide (50% aqueous solution, 11.5 mmol). After stirring for 4—5 h, evaporation of the volatile was performed without heating. The pure $\text{C}_4\text{H}_8\text{ONCS}_2\text{Na}$ was obtained by recrystallization from the solution of CH_3CN . Yield: 92%.

Preparation of the Ni(II) complex $\text{Ni}(\text{C}_4\text{H}_8\text{ONCS}_2)_2$

To a heated aqueous solution of $\text{C}_4\text{H}_8\text{ONCS}_2\text{Na}$ (0.1 mol) was added an aqueous solution of Ni perchlorate [$\text{Ni}(\text{ClO}_4)_2$, 0.05 mol] with stirring. A green precipitate was collected by filtration, washed with water, and dried over P_2O_5 . Single crystals suitable for X-ray analysis were obtained by recrystallization from

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CH₃COCH₃ solution. It was collected and submitted for elemental analysis. The C, H and N contents were determined by elemental analysis. Anal. C₁₀H₁₆N₂NiO₂S₄. Calcd; C, 31.32; H, 4.18; N, 7.31. Found; C, 31.07; H, 4.01; N, 7.65.

Physical measurements

Elemental analyses were performed on a Perkin Elmer 240C analytical instrument. The IR spectra were recorded in the 4000—400 cm⁻¹ region using KBr pellets on a Bruker VECTOR 22 FT-IR spectrometer. Thermal analyses were performed in nitrogen gas with a Shimadzu TGA-50 (10°C/min).

X-ray structure determination

A summary of the key crystallographic information is given in Table 1. Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed

in Table 2. The selected crystal of the title compound was mounted on a Bruker P4 diffractometer. Reflection data and reflections for the unit cell determination were measured at 20°C using Mo K_α radiation ($\lambda = 0.071073$ nm) with a graphite monochromator. The technique used was ω -scan with θ limits of $1.98^\circ < \theta < 24.96^\circ$. Usual L_p and empirical absorption correction were carried out by using the SADABS 8 program. The structure of the title compound was solved by direct method and refined by full matrix least squares on F^2_{obs} by using the SHELXTL⁹ software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located from the difference map and refined isotropically. The final conventional $R_1 = 0.0404$ and $wR_2 = 0.0823$ for 1273 reflections with $I > 2\sigma(I)$; the weighting scheme, $w = 1/[\sigma^2(F^2) + (0.0429P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics was created using SHELXTL.⁹ Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography.¹⁰

Table 1 Crystallographic data for C₁₀H₁₆N₂NiO₂S₄

Formula	C ₁₀ H ₁₆ N ₂ NiO ₂ S ₄
<i>M</i>	383.2
Crystal size (mm)	0.02 × 0.16 × 0.19
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions (nm, °)	<i>a</i> = 0.4288(1), α = 90 <i>b</i> = 2.0526(4), β = 97.43(3) <i>c</i> = 0.8333(2), γ = 90
Volume (nm ³), <i>Z</i>	0.7273(3), 2
<i>D</i> _c (g/cm ³)	1.750
μ (mm ⁻¹)	1.905
<i>F</i> (000)	396
Temperature (K)	293(2)
Radiation, λ (nm)	Mo K _α , 0.071073
θ range for data collection (°)	1.98 to 24.96
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 ≤ <i>h</i> ≤ 5, 0 ≤ <i>k</i> ≤ 24, -9 ≤ <i>l</i> ≤ 9
Unique reflections	1448
Reflections with $I > 2\sigma(I)$	1273 [<i>R</i> (int) = 0.0340]
Goodness of fit on <i>F</i> ²	0.998
Final <i>R</i> indices	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.0823
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1257, <i>wR</i> ₂ = 0.1036
Residual extreme in final difference map (e/nm ³)	413, -339

Table 2 Atomic coordinates and thermal parameters for $C_{10}H_{16}N_2NiO_2S_4$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} ($\times 10^5$ nm ²)
Ni(1)	0	0	0	33(1)
S(2)	1.717(4)	0.016(1)	-2.377(2)	43(1)
S(1)	1.093(4)	1.036(1)	-0.313(2)	43(1)
N(1)	3.296(1)	1.197(2)	-3.159(5)	30(1)
C(2)	4.348(4)	0.965(3)	-4.665(6)	39(2)
C(1)	2.224(3)	0.798(2)	-2.113(6)	29(1)
C(5)	3.989(6)	1.886(2)	-2.796(6)	40(2)
O(1)	4.359(1)	2.084(2)	-5.633(5)	48(1)
C(4)	3.006(5)	2.299(3)	-4.259(7)	44(2)
C(3)	3.343(6)	1.438(3)	-6.018(7)	48(2)

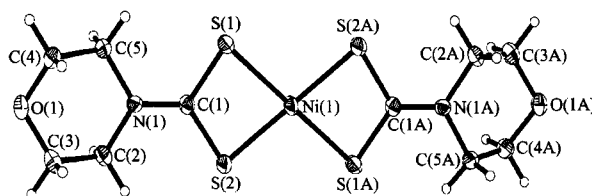
Results and discussion

Description of the structure

The structure of the title compound $Ni(C_4H_8ONCS_2)_2$ is built up of centro-symmetric monomeric entity. Fig. 1 shows a perspective view of the monomeric unit with the atomic numbering scheme. Selected bond distances and angles are listed in Table 3.

The coordination sphere of the Ni(II) ions is best described as a slightly distorted square-planar one. The two dithiocarbamate ligands coordinate to one Ni atom through the S atoms. The nickel atom is situated on a

center of symmetry and thus the asymmetric unit consists of a nickel atom and a single morpholine dithiocarbamate ligand. The sulphur atoms of the chelated ligands form an approximately square planar array [$S(1)-Ni-S(2)$, $78.86(5)^\circ$] around nickel. The bond lengths of $S(1)-Ni$ and $S(2)-Ni$ are 0.2199(1) and 0.2201(1) nm, respectively, and the bond angles of $S(1)-Ni-S(2)$ and $S(1)-Ni-S(2A)$ are $78.86(5)^\circ$ and $101.14(5)^\circ$, respectively. All these parameters are in close agreement with those reported before.^{11,12} The $Ni-S(1)$ bond length is shorter than that of $Ni-S(2)$ which can be interpreted on the basis of the interaction effect between the $S(1)$ and Ni atom. The ligand "bite" angle $S-C-S$ has a mean value of $110.5(3)^\circ$. The $C-S$ bond distances of 0.1695(5)—0.1706(5) nm agree very well with those in related compounds.¹³ The $N(1)-C(1)$ bond distance [0.1321(6) nm] is shorter than the other $N-C$ bond distances which are indicative of considerable double-bond character. The $C-C$ and $C-O$ bond

**Fig. 1** Molecular structure for $Ni(C_4H_8ONCS_2)_2$ with the atomic numbering scheme.**Table 3** Bond lengths (nm) and angles ($^\circ$) for $C_{10}H_{16}N_2NiO_2S_4$

$Ni(1)-S(1A)$	0.2199(5)	$N(1)-C(1)$	0.1321(6)
$Ni(1)-S(1)$	0.2199(5)	$N(1)-C(2)$	0.1466(6)
$Ni(1)-S(2)$	0.2201(2)	$N(1)-C(5)$	0.1469(6)
$Ni(1)-S(2A)$	0.2201(2)	$O(1)-C(4)$	0.1418(6)
$S(2)-C(1)$	0.1696(5)	$O(1)-C(3)$	0.1421(7)
$S(1A)-Ni(1)-S(1)$	180.01(9)	$C(1)-N(1)-C(2)$	122.4(4)
$S(1A)-Ni(1)-S(2)$	101.14(5)	$C(1)-N(1)-C(5)$	122.6(4)
$S(1)-Ni(1)-S(2)$	78.86(5)	$C(2)-N(1)-C(5)$	114.3(4)
$S(1A)-Ni(1)-S(2A)$	78.86(5)	$N(1)-C(2)-C(3)$	110.0(5)
$S(1)-Ni(1)-S(2A)$	101.14(5)	$N(1)-C(1)-S(2)$	125.1(4)
$S(2)-Ni(1)-S(2A)$	180.00(8)	$N(1)-C(1)-S(1)$	124.5(4)
$C(1)-S(2)-Ni(1)$	85.44(8)	$S(2)-C(1)-S(1)$	110.5(3)
$C(1)-S(1)-Ni(1)$	85.26(8)	$N(1)-C(5)-C(4)$	110.4(4)
$C(4)-O(1)-C(3)$	109.1(4)	$O(1)-C(3)-C(2)$	112.5(5)

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

lengths are normal.

The morpholine ring adopts a normal ${}^4C^1$ chair conformation. The atoms of Ni, C(1), C(1A), C(2), C(2A), N(1), N(1A), S(1), S(1A), S(2) and S(2A) are coplanar (plane 1), with the maximum deviation of 0.0024(1) nm. The atoms of C(2), C(3), C(4) and C(5) are coplanar (plane 2). The dihedral angle between plane 1 and plane 2 is 20.79(3)°.

IR spectroscopy

The IR spectra of the title compound exhibit the characteristic absorption, the strong band 1494.6 cm^{-1} , attributed to the $\nu(\text{C}-\text{N})$ stretching vibration, and the band in the 877.0 cm^{-1} , belonging to the $\nu(\text{C}-\text{S})$ stretching vibration.¹⁴ The band 1018.3 cm^{-1} in the metal complexes is assigned to asymmetric stretching mode of the CS_2 group. This band must be highly coupled with other modes and is very sensitive to environmental change.¹⁵ The average value of $\nu_{\text{as}}(\text{CS}_2)$ and $\nu_{\text{s}}(\text{CS}_2)$ at about 653.4 cm^{-1} .¹⁴ Accordingly, this band has been used to distinguish between disulfur chelation and unisulfur coordination. With disulfur chelation a single band is usually found,¹⁶ whereas when unisulfur coordination occurs, this band is split. The asymmetric band in our case is unsplit, indicating the bidentate modes of the dithio-ligands.

Thermal analysis

Thermal analysis curves of the title compound are shown in Fig. 2. The complex first undergoes fusion at temperatures ranging from 231.22 to 311.87°C.

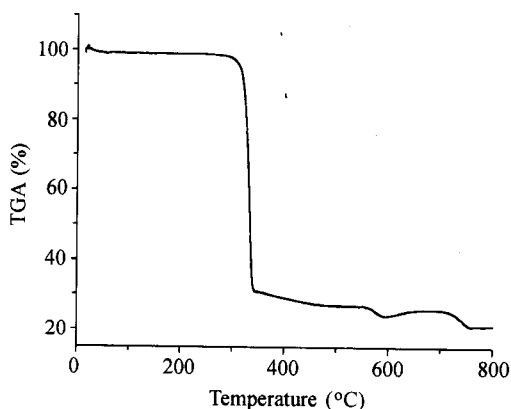


Fig. 2 TG diagram of the complex.

At 354°C, the complex decomposed quickly, forming NiS_2 (Found: 68.85%; Calcd.: 67.94%). With the increase of the temperature, the complex loses weight slowly at temperatures ranging from 359.06 to 766.89°C, and the lost weight is 80.2%, which indicates the final product is metal Ni (Calcd.: 84.4%).

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