Nolwazi Solomane, Peter A. Ajibade and Bernard Omondi*

Crystal structure of sodium morpholine-4-carbodithioate, (C₅H₁₂NNaO₃S₂)

<https://doi.org/10.1515/ncrs-2018-0512>

Received November 19, 2018; accepted February 14, 2019; available online March 26, 2019

Abstract

C₅H₁₂NNaO₃S₂, monoclinic, *P*2₁/*c* (no. 14), *a* = 28.8222(3) Å, *b* = 5.6782(3) Å, *c* = 12.3810(9) Å, β = 102.074(2)°, *V* = 1987.43(17) Å³, *Z* = 8, *R*_{gt}(*F*) = 0.0269, *wR*_{ref}(*F*²) = 0.0591, *T* = 100(2) K.

CCDC no.: 1855486

The asymmetric unit of the title crystal structure is shown in the figure (The disorder in the morpholine moieties is omitted for clarity.). Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized by dispersing (4.33 mL, 50 mmol) of morpholine into 20 mL of diethyl ether and stirred for 10 minutes. Followed by the addition of 20 mL of an ice cold methanolic solution of sodium hydroxide (2.00 g, 50 mmol) and stirred for 15 minutes at an ice-cold temperature. To this mixture, cold carbon disulfide (3 mL, 50 mmol) was added dropwise. The mixture was stirred for 4 h while maintaining an ice-cold temperature resulting in a formation of white precipitate which was collected by filtration. The

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.36 × 0.23 × 0.14 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.55 mm ^{−1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
θ _{max} , completeness:	27.4°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	31639, 4506, 0.024
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 4308
<i>N</i> (<i>param</i>) _{refined} :	150
Programs:	Bruker programs [1], SHELX [2], WinGX and ORTEP [3]

product obtained was rinsed with diethyl ether and dried in a desiccator. The crystals of the title compound were formed after four days of extracting the filtrate with diethyl ether. White powder. Yield = 61%. m.p. 308.4–310.3 °C. ¹H NMR D₂O: δ = 3.77 (4H, t, N–CH₂), 4.36 (4H, t, O–CH₂). ¹³C NMR D₂O: δ = 51.40 (N–CH₂), 66.13 (O–CH₂), 209.36 (C–SSNa). IR ν(cm^{−1}): 972 (C–S), 1108 (C=S), 1414 (C–N). MS (*m/z*): 162.0045 [*M*⁺].

Experimental details

Crystal evaluation and data collection were done on a Bruker Smart APEX2 diffractometer [1]. The structure was solved by the direct method using the SHELXS [2] program and refined using SHELXL [2]. The visual crystal structure information was obtained using ORTEP-3 [3] system software. All hydrogen atoms were placed in idealized positions and refined in riding models with *U*_{iso} assigning values of 1.2 times those of their parent atoms and the distances of C–Hs were constrained to 0.99 Å for all the methylene H atoms and 0.84 Å for water hydrogens.

Both morpholine moieties are disordered over two positions (Table 2).

Discussion

Dithiocarbamate ligands are known to be flexible ligands that are able to form diverse types of complexes and be able to stabilize transition metal in various oxidation states [4, 5]. They may possess electrochemical and optical properties because of their redox behaviour and strong coordination ability [6]. They are known to be planar and sterically non-demanding

*Corresponding author: Bernard Omondi, University of KwaZulu-Natal, School of Chemistry and Physics, PO Box X01, Pietermaritzburg Campus, Scottsville, Pietermaritzburg 3209, South Africa, e-mail: owaga@ukzn.ac.za

Nolwazi Solomane and Peter A. Ajibade: University of KwaZulu-Natal, School of Chemistry and Physics, PO Box X01, Pietermaritzburg Campus, Scottsville, Pietermaritzburg 3209, South Africa

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
S1	0.55623(2)	0.03105(6)	0.78588(3)	0.01240(8)
O1	0.45297(4)	−0.09325(19)	0.91778(9)	0.0155(2)
S2	0.63255(2)	0.23405(7)	0.96360(3)	0.01908(9)
S4	0.94367(2)	−0.03262(6)	1.23051(3)	0.01196(8)
S3	0.86773(2)	−0.24153(6)	1.33344(3)	0.01535(8)
Na1	0.49327(2)	0.25887(10)	0.91592(4)	0.01334(12)
Na2	0.99301(2)	0.24134(10)	1.07727(4)	0.01347(12)
O2	0.54519(4)	0.5878(2)	0.94798(9)	0.0150(2)
O3	0.95269(4)	0.59302(19)	1.03569(9)	0.0151(2)
O4	1.04453(4)	−0.0892(2)	1.09677(9)	0.0155(2)
O1A ^a	0.71454(6)	−0.3683(3)	0.76431(14)	0.0275(4)
C2A ^a	0.66508(7)	−0.3968(4)	0.72608(17)	0.0224(4)
H2AA ^a	0.651540	−0.473359	0.784375	0.027*
H2AB ^a	0.659231	−0.501320	0.660638	0.027*
C1A ^a	0.64031(8)	−0.1632(5)	0.69550(19)	0.0179(5)
H1AA ^a	0.652399	−0.088940	0.634480	0.022*
H1AB ^a	0.605753	−0.188696	0.670403	0.022*
N1A ^a	0.64941(6)	−0.0095(3)	0.79245(16)	0.0150(4)
C1	0.61594(5)	0.0703(3)	0.84542(12)	0.0172(3)
C3A ^b	0.72386(8)	−0.2202(5)	0.85912(19)	0.0268(5)
H3AA ^b	0.758564	−0.200031	0.884208	0.032*
H3AB ^b	0.711654	−0.296028	0.919601	0.032*
C4A ^b	0.70071(7)	0.0202(4)	0.83457(18)	0.0221(4)
H4AA ^b	0.706321	0.116435	0.902748	0.027*
H4AB ^b	0.714882	0.103137	0.778969	0.027*
C7 ^b	0.88425(5)	−0.0648(3)	1.23605(13)	0.0200(3)
N1B ^b	0.6461(3)	−0.1046(17)	0.8302(6)	0.0229(17)
C3B ^b	0.6741(3)	−0.1908(19)	0.6646(7)	0.033(2)
H3A ^b	0.668880	−0.283507	0.595410	0.039*
H3B ^b	0.670723	−0.021693	0.645134	0.039*
O1B ^b	0.7211(2)	−0.2362(17)	0.7295(6)	0.0385(19)
C4B ^b	0.7287(3)	−0.083(2)	0.8248(7)	0.035(2)
H12A ^b	0.761660	−0.100481	0.867208	0.042*
H12B ^b	0.724018	0.083056	0.800456	0.042*
C5B ^b	0.6959(3)	−0.1413(18)	0.8945(7)	0.032(2)
H13A ^b	0.701842	−0.039784	0.960984	0.038*
H13B ^b	0.700271	−0.307453	0.918704	0.038*
C2B ^b	0.6398(3)	−0.2571(19)	0.7294(8)	0.023(2)
H15A ^b	0.644200	−0.424523	0.751503	0.027*
H15B ^b	0.607240	−0.237908	0.684652	0.027*
O2A ^c	0.7808(2)	0.3381(8)	1.0415(4)	0.0241(8)
N2A ^c	0.85009(7)	0.0104(4)	1.15107(17)	0.0150(4)
C5A ^c	0.79895(8)	−0.0287(5)	1.1431(2)	0.0213(5)
H5AA ^c	0.793880	−0.112700	1.209790	0.026*
H5AB ^c	0.786137	−0.127670	1.077873	0.026*
C8A ^c	0.85855(8)	0.1566(5)	1.0594(2)	0.0183(5)
H8AA ^c	0.848921	0.069446	0.988992	0.022*
H8AB ^c	0.892800	0.193185	1.070167	0.022*
C7A ^c	0.83047(8)	0.3831(5)	1.0539(2)	0.0223(5)
H7AC ^c	0.841840	0.474885	1.122310	0.027*
H7AD ^c	0.835826	0.478690	0.990767	0.027*
C6A ^c	0.77320(12)	0.2054(7)	1.1329(3)	0.0238(7)
H6AC ^c	0.738765	0.176893	1.124981	0.029*
H6AD ^c	0.784221	0.297518	1.201369	0.029*
N2B ^d	0.85459(12)	0.1221(7)	1.1920(3)	0.0129(7)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C6B ^d	0.86342(15)	0.2834(9)	1.1047(4)	0.0178(9)
H2C ^d	0.895502	0.255411	1.090399	0.021*
H2D ^d	0.861639	0.448896	1.128646	0.021*
C7B ^d	0.82628(16)	0.2389(9)	1.0006(4)	0.0217(9)
H9AA ^d	0.831825	0.346724	0.941786	0.026*
H9AB ^d	0.829497	0.075408	0.975394	0.026*
C9B ^d	0.80589(14)	0.1546(8)	1.2098(3)	0.0172(8)
H6AA ^d	0.802222	0.316016	1.237083	0.021*
H6AB ^d	0.799714	0.041440	1.265959	0.021*
C8B ^d	0.7710(2)	0.1153(12)	1.1023(5)	0.0211(12)
H7AA ^d	0.773330	−0.049684	1.078147	0.025*
H7AB ^d	0.738366	0.141104	1.113547	0.025*
O2B ^d	0.7800(4)	0.2726(15)	1.0174(8)	0.0224(15)
H1A	0.4492(7)	−0.179(4)	0.8673(17)	0.026(5)*
H3C	0.9494(7)	0.679(4)	1.0831(17)	0.026(5)*
H2A	0.5467(7)	0.691(4)	0.9045(17)	0.028(5)*
H4A	1.0458(7)	−0.198(4)	1.1437(18)	0.033(6)*
H2B	0.5699(8)	0.514(4)	0.9506(16)	0.030(6)*
H4B	1.0680(8)	−0.015(4)	1.1179(17)	0.034(6)*
H3D	0.9294(8)	0.608(4)	0.9877(18)	0.032(6)*
H1B	0.4288(8)	−0.110(4)	0.9439(18)	0.039(6)*

Occupancies: a = 0.8, b = 0.2, c = 0.65, d = 0.35.

ligands that can be automatically changed by having choices of substituents [7]. Their functionalization of substituents on the nitrogen atom of the dithiocarbamate moiety, can result in various complex structures through secondary interactions hence desirable physical properties [8]. The ease of formation of metal complexes is due to the electron delocalization around the N(CSS)- moiety which is also transferred to the metal centre [9]. This ability is recognized to the approval of dithiocarbamates and thioureide tautomers [10]. In dithiocarbamates, the sulfur atoms act as soft donor atoms containing a lone pair of electron localized on nitrogen (*sp*³) resulting in pyramidal arrangement of substituents. In thioureide systems there are donor ligands which are planar with lone pair of electron localized in the backbone of carbon-nitrogen bond and onto the sulfur atoms [10]. Dithiocarbamate ligands have been widely used in coordination chemistry due to diverse applications, for example used in dyes, agricultural and pharmaceutical industries and to chelate with heavy metals [11–13].

Dithiocarbamate ligands are mostly synthesized from nucleophilic addition reaction of primary or secondary amines with carbon disulfide in the presence of a strong base i.e. sodium/ potassium hydroxide acting as a proton acceptor [14]. The formation of these compounds is often accompanied by release of heat, hence the syntheses are carried out at low temperatures [15]. The title compound was as such prepared by the reaction morpholine 4-dithiocarbamate with sodium hydroxide in ethanol.

The asymmetric unit of the title compound contains two fragments of two chains of coordination polymers (see the figure). The fragments contain a morpholine 4-dithiocarbamate moiety and two water molecules coordinated to a sodium centre. The coordination of the two water molecules to the Na center results in four member metallacycles connected in alternating orthogonal fashion in the *b* crystallographic direction. Two S atoms from two morpholine moieties also in the same chains occupy the other coordination sites such that adjacent chains have the O containing sides of the chair conformed morpholine facing each other. The interaction between the sodium cation and water molecules does not disturb the geometric conformation of the ligand [16]. The S—Na bond distances are 3.0291(7) Å, while the S—C ones are 1.7151(15) Å and 1.7390(15) Å indicating a tendency towards a double bond character of electron density in the S—C—S group [17]. The C—S—Na bond angle is 132.42(5)°, while the S—C—S bond angle is 120.40(8)° and is similar to what is observed for similar complexes.

Acknowledgements: We acknowledge the University of KwaZulu-Natal and National Research Foundation of South Africa for financial support for Ekemini Akpan and Sizwe J. Zamisa.

References

1. Bruker. APEX3, SAINT-Plus, XPREP. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Farrugia, L. J.: WinGX and ORTEP for Windows. *Appl. Crystallogr.* **45** (2012) 849–854.
4. Al-Hasani, T. J.; Al-Taie, M. K.: Synthesis, structural and antibacterial study of some metal ion dithiocarbamate-azo complexes. *J. Al-Nahrain University-Scie.* **18** (2015) 1–12.
5. Beyramabadi, S.; Morsali, A.; Vahidi, S.: Dft characterization of 1-acetylpiperazinyl-dithiocarbamate ligand and its transition metal complexes. *J. Struct. Chem.* **53** (2012) 665–675.
6. Tiwari, S.; Reddy, K.; Bajpai, A.; Khare, K.; Nagaraju, V.: Synthesis and characterization of bisdithiocarbamates from weak nitrogen bases and its metal complexes. *Int. Res. J. Pure. Appl. Chem.* **7(2)** (2015) 78–91.
7. Venugopal, K.; Rameshbabu, K.; Sreeramulu, J.: Synthesis and characterization of (novel heterocyclic) 3-amino-9-ethyl carbazole dithiocarbamate [aeczdtc] ligand and its metal complexes. *Der. Pharma. Chemica.* **7** (2015) 252–60.
8. Manar, K. K.; Yadav, M. K.; Drew, M. G.; Singh, N.: Influence of functionalities over polymer, trimer, dimer formation and optical properties of cadmium dithiocarbamates. *Polyhedron* **117** (2016) 592–599.
9. Vojta, D.; Višnjevac, A.; Leka, Z.; Kosović, M.; Vazdar, M.: Temperature-induced release of crystal water in the Co, Mo and Pt complexes of N,N-diacetatedithiocarbamate. FTIR spectroscopy and quantum chemical study. *J. Mol. Struct.* **1103** (2016) 245–253.
10. Hogarth, G.: Metal-dithiocarbamate complexes: chemistry and biological activity. *Mini Rev. Med. Chem.* **12** (2012) 1202–1215.
11. Rani, P. J.; Thirumaran, S.; Ciattini, S.: Synthesis and characterization of Ni(II) and Zn(II) complexes of (furan-2-yl)methyl (2-(thiophen-2-yl)ethyl) dithiocarbamate (ftpedtc): X-ray structures of [Zn(ftpedtc)₂(py)] and [Zn(ftpedtc)Cl(1,10-phen)]. *Spectrochim. Acta A* **137** (2015) 1164–1173.
12. Abu-El-Halawa, R.; Zabin, S. A.: Removal efficiency of Pb, Cd, Cu and Zn from polluted water using dithiocarbamate ligands. *J. Taibah. Univ. Sci.* **11** (2017) 57–65.
13. Hou, X.; Li, X.; Hemit, H.; Aisa, H. A.: Synthesis, characterization, and antitumor activities of new palladium (ii) complexes with 1-(alkyldithiocarbonyl)-imidazoles. *J. Coord. Chem.* **67** (2014) 461–469.
14. Andrew, F. P.; Ajibade, P. A.: Metal complexes of alkyl-aryl dithiocarbamates: Structural studies, anticancer potentials and applications as precursors for semiconductor nanocrystals. *J. Mol. Struct.* **1155** (2018) 843–855.
15. Nabipour, H.: Synthesis of a new dithiocarbamate cobalt complex and its nanoparticles with the study of their biological properties. *Int. J. Nano Dimension* **1** (2011) 225–232.
16. Amim, R. S.; Oliveira, M. R.; Perpétuo, G. J.; Janczak, J.; Miranda, L. D.; Rubinger, M. M.: Syntheses, crystal structure and spectroscopic characterization of new platinum (II) dithiocarbamate complexes. *Polyhedron* **27** (2008) 1891–1897.
17. Andrew, F. P.; Ajibade, P. A.: Synthesis, characterization and anticancer studies of bis (1-phenylpiperazine dithiocarbamate) Cu(II), Zn(II) and Pt(II) complexes: Crystal structures of 1-phenylpiperazine dithiocarbamate-S,S' Zn(II) and Pt(II). *J. Mol. Struct.* **1170** (2018) 24–29.