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NOTE

Synthesis and Crystal Structure of *o*-Methoxyethyldithiocarbonato Nickel(II) Complex involving Tetramethylethylenediamine

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A new nickel(II) complex of type [Ni(xan)$_2$(tmen)] (**1**) (xan = *o*-methoxyethyldithiocarbonate, tmen = tetramethylethylenediamine) has been synthesized and characterized by single crystal X-ray diffraction analysis. The compound crystallizes in orthorhombic space group Fdd2 with a = 13.956 (3), b = 38.342 (6), c = 8.1611 (12) Å, α = 90, β = 90, γ = 90°, V = 4367.2(12) Å^3, Z = 8, F(000) = 2016.0, D$_c$ = 1.452 Mg/m^3, μ = 1.291 mm^{-1}. Ni(II) ion is in distorted octahedral geometry. The xanthate ligand acted as isobidentate.

Keywords: Nickel, Synthesis, *o*-Methoxyethyldithiocarbonate, Crystal.

The chemistry of xanthates (dithiocarbonates) has attracted increased attention due to their diverse applications such as fungicides, pesticides, vulcanizes and corrosion inhibitors [1-4]. These are known to exhibit antitumor and antioxidant properties [5,6]. Sodium and potassium xanthate have antitodal effects in acute mercurial poisoning [7]. Xanthates have been shown to inhibit the replication of both DNA and RNA viruses *in vitro* [8]. *o*-Alkyldithiocarbonate forms a chelate with most of the transition elements and has proven to be a versatile chelating agent for the separation and extraction of metals in analytical chemistry and mineral floating [9,10]. These ligands can coordinate to metal ions in a monodentate, isobidentate, anisobidentate or bridging fashion. Transition metal complexes of xanthate have been used as precursors for synthesis of semiconductor nanoparticles [11]. In this report, we report the synthesis and crystal structure of the [Ni(xan)$_2$(tmen)] (**1**) (xan = *o*-methoxyethyldithiocarbonate, tmen = tetramethylethylenediamine).

Crystal structure determination: Single crystal of the title complex **1** suitable for X-ray diffraction analysis was grown by slow evaporation of the acetone solution. The crystal of **1** with dimensions of 0.36 mm × 0.18 mm × 0.12 mm was mounted on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073) at 100.0(2) K. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 data using SHELXL [12].

Synthesis: To ethanolic solution (20 mL) of NiCl$_2$·6H$_2$O (0.48 g, 2 mmol) and tetramethylethylenediamine (0.24 g, 2 mmol) was added ethanolic solution (20 mL) of potassium *o*-methoxyethyldithiocarbonate (0.77 g, 4 mmol). The mixture was stirred for 1.5 h. The solvent was evaporated and the residue was recrystallized from acetone. Elemental analysis (%): Found: C, 35.04; H, 6.48; N, 5.71. Calcd.: C, 35.23; H, 6.33; N, 5.87.

Ni(II) complex was obtained by reaction of NiCl$_2$·6H$_2$O with tmen and xanthate in ethanol. The product dissolved in polar solvents such as ethanol, methanol and acetone. The elemental analysis shows that its composition is [Ni(C$_4$H$_7$O$_2$S$_2$)$_2$(C$_6$H$_{16}$N$_2$)] which was confirmed by the crystal structure analysis.

IR spectra and magnetic moment: IR spectrum of the compound exhibits characteristic strong bands at 1176 and 1056 cm^{-1} which are assigned to ν(C-O-C). The band appeared at 802 cm^{-1} is attributed to ν(C-S) vibration. The single band of ν(C-S) indicates that the xanthate is bonded to the metal in a bidentate fashion. Magnetic moment of **1** is 3.13 BM which is consistent with two unpaired electrons of octahedral Ni(II) complex.

Crystal structure: The molecular structure of the Ni(II) complex is shown in Fig. 1. Details of the data collection and refinements are given in Table-1. Selected bond lengths and angles are listed in Table-2. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-square refinements based on F^2. The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

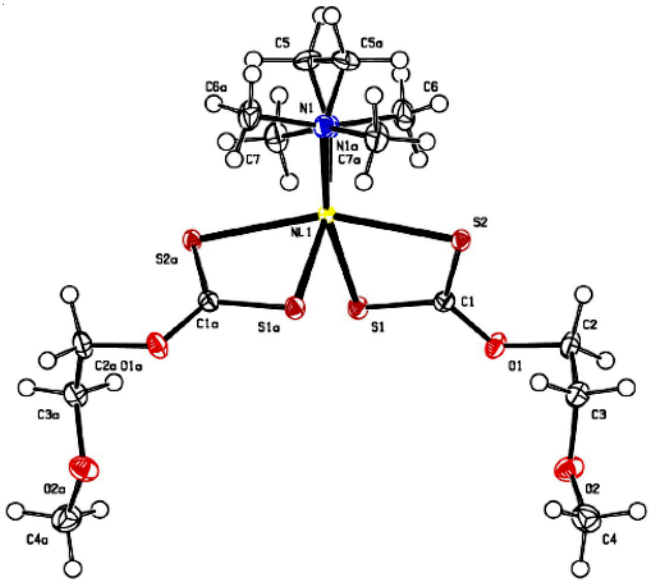

Fig. 1. Molecular structure of the title compound with 50 % probablity displacement ellipsoids

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT FOR Ni(II) COMPLEX

Chemical formula	$C_{14}H_{30}N_2O_4S_4Ni$
Formula weight	477.35
Cell system, space group	Orthorhombic, Fdd2
a (Å)	13.956(3)
b (Å)	38.342(6)
c (Å)	8.1611(12)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	4367.2(12)
Z	8
Dc (Mg m^{-3})	1.452
μ (mm^{-1})	1.291
Crystal size (mm)	0.36 × 0.18 × 0.12
2θ range for data collection	5.88 to 63.694°
Index ranges	-20 ≤ h ≤ 19, -56 ≤ k ≤ 55, -12 ≤ l ≤ 12
Reflection collected	27356
Independent reflections	3708 [R_{int} = 0.0564, R_{sigma} = 0.0423]
Data/restraints/parameters	3708/1/117
F (000)	2016.0
Goodness-of-fit on F^2	1.014
R1 [I > 2σ(I)]	R1 = 0.0273,
wR2 [I > 2σ(I)]	wR_2 = 0.0492
R1 (all data)	R_1 = 0.0312,
wR2 (all data)	wR_2 = 0.0504
Min. and max. resd. dens. [e/Å^3]	0.27/-0.25

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE COMPLEX

Bond length (Å)			
Ni1-S1	2.4582(6)	Ni-N1A	2.1711(19)
Ni1-S1A	2.4582(6)	C1-S1	1.699(2)
Ni1-S2	2.4935(6)	C1-S2	1.707(2)
Ni1S2A	2.4934(6)	O1-C1	1.344(3)
Ni1-N1	2.1711(19)	O2-C1	1.463(3)
Bond angle (°)			
S1Ni1S2	72.84(2)	S1NiS1A	92.17(3)
S1ANi1S2A	72.84(2)	S2Ni1S2A	158.33(3)
N1Ni1N1A	84.01(11)	N1Ni1S1	93.09(6)
S1C1S2	119.35(13)	N1Ni1S1A	167.62(5)
O1C1S1	116.36(16)	O1C1S2	124.29(17)

X-ray crystallography indicates that the Ni(II) ion is coordinated by four sulfur atoms (S1, S2, S1A, S2A) from two different xantahte ligands and two nitrogen atoms (N1, N1A) from tmen forming distorted octahedral geometry. The Ni-S bond lengths range from 2.4582(6) to 2.4935(6) Å, indicating the isobidentate nature of the xanthate ligands. The nearly identical values of C-S lengths (1.699(2)-1.707(2) Å) is indication of delocalization of CS_2^- electrons.

Supplementary material

CCDC 1038468 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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