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Synthesis, X-Ray Crystal Structure and Electrical Conduction Properties of a New Linear-Chain Mixed-Valence (μ-IODO)-Tetrakis (Dithioacetato) Di-Nickel: Ni_2 $(CH_3$ $CS_2)_4$ I

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SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND ELECTRICAL CONDUCTION PROPERTIES OF A NEW LINEAR-CHAIN MIXED-VALENCE (μ-IODO)-TETRAKIS(DITHIOACETATO)DI-NICKEL: $Ni_2(CH_3CS_2)_4I$.

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Abstract. (μ-Iodo)tetrakis(dithioacetato)di-nickel has been synthesized and characterized. The compound crystallizes in the monoclinic space group P2/n, with the unit-cell parameters: a=8.934(2), b=8.382(2), c=12.492(2) Å and β=106.21°. The crystal structure consists of linear chains of $[Ni_2S_8]$---I---$[Ni_2S_8]$ -- , stacking along the crystallographic b axis. The observed electrical conductivity is typical of a semiconductor, i.e. 5×10^{-6} Ω^{-1} cm^{-1}, with a very low activation parameter, E_a = 0.07 eV; a " hopping type "mechanism for the electrical conductivity is suggested.

INTRODUCTION

Several nickel-triad metal(II) derivatives of dithiocarboxylic acids, RCSSH, show columnar structure[1,2], and they undergo oxidative addition with halogens[3]. Tetrakis(dithioacetato)di-platinum(II), $Pt_2(CH_3CS_2)_4$, reacts with iodine to give two compounds. One of them having formula $Pt_2(CH_3CS_2)_4I$, is a linear chain mixed-valence platinum compound, where the dimeric $[Pt_2S_8]$ units are bridged by iodine atoms, stacked along the crystallographic b axis (C2/c space group). This compound is peculiar, because it is a semiconductor with a maximum powder electrical conductivity at r.t. of 7×10^{-3} Ω^{-1} cm^{-1}. With the aim to obtain new extended linear-chain compounds with sulphur and selenium donor ligands, we studied the reaction of the analogous nickel derivative with halogens. Here we present the synthesis, the X-ray crystal structure and the physical properties of the product obtained by reaction of $Ni_2(CH_3CS_2)_4$ with iodine.

RESULTS AND DISCUSSION.

Tetrakis(dithioacetato)di-nickel(II) reacts with iodine in the ratio 1:1/2 to give a crystalline black product of formula $Ni_2(CH_3CS_2)_4I$. The compound has been characterized by elemental analysis and *i.r.spectroscopy*. Anal.calcd. for $C_8H_{12}S_8Ni_2I$, M.W.= 608.88, : C = 15.78%; H = 1.97%; S = 42.12%; Ni = 19.29%; I =20.84 %. Found :C =15.76%; H =1.90%; S = 42.01%; Ni = 19.09%;I =21.02%. The infrared spectra of the starting material and that of the oxidized one are similar and the assignements have been made by comparison, as has been previously done with similar palladium and platinum derivatives [1,2]. The compound is diamagnetic,insoluble in polar solvents and slightly soluble in CS_2 or CH_2Cl_2 . It crystallizes in the monoclinic space group P2/n,with the following unit-cell parameters : a = 8.934(2), b = 8.382(2), c = 12.492(2) Å and β = 106.21°,Z = 2,D_m = 2.23 g cm^{-3},D_c = 2.25 g cm^{-3}. The crystal structure consists of infinite chains of $\cdots[Ni_2S_8]\text{-}I\text{-}[Ni_2S_8]\text{-}I\text{-}\cdots$,as reported in Figure 1. The Ni-Ni distance in the dimer is 2.514(3) Å ,0.05 Å shorter than the corresponding distance in the unoxidized material [4]. The Ni - I distances are 2.928(4) and 2.940(4) Å and all the Ni and I atoms lie on the twofold axes. The observed shorter Ni - Ni distance in the title compound can be related to the change of the oxidation state of the metal ion.

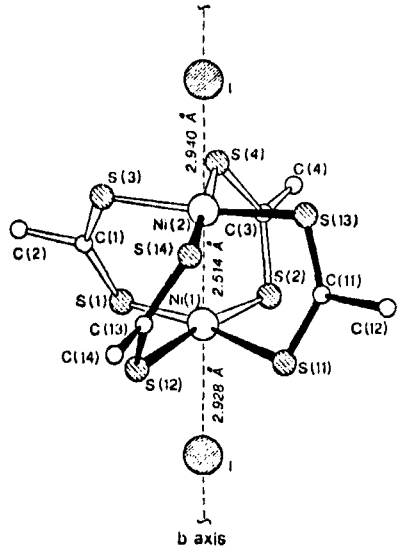

FIGURE 1. Atomic arrangement of the title compound showing the Ni and I sequence along the b axis .

X-RAY PHOTOELECTRON DATA.

X-ray photoelectron spectroscopy provides useful information on

the electronic structure of the material. In Figure 2 are reported Ni ($2p_{3/2}$,$2p_{1/2}$) spectra of $Ni_2(CH_3CS_2)_4$ and $Ni_2(CH_3CS_2)_4I$ and complete data are reported in Table 1. The binding energies and line widths of both compounds are in agreement with the literature data[5], and they do not differ significantly,except for a small energy shift. The full width at half-maximum, fwhm , is the same for all the compound,i.e. = 2eV in value,suggesting equivalent nickel atoms present in the dimer. The energy shift takes into account the change of the oxidation state of the metal. The absence of " shake up[6] " satellites is in agreement with the observed diamagnetism .

TABLE 1 . X-ray photoelectron spectroscopic data for $Ni_2(CH_3CS_2)_4$ and $Ni_2(CH_3CS_2)_4I$. *

material	Ni $2p_{3/2}$	S 2p	halogen	
$Ni_2(CH_3CS_2)_4$	854.80 (2.0)	162.70		
$Ni_2(CH_3CS_2)_4I$	855.20 (2,0)	162.60	619.10	630.80

* Binding energies in eV, fwhm in parenthesis.

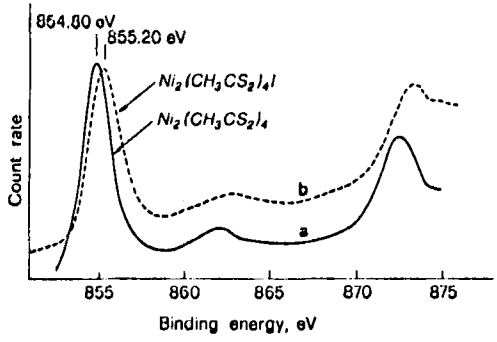

FIGURE 2. X-ray photoelectron spectra (Ni region).

SALIENT FEATURES OF $Ni_2(CH_3CS_2)_4I$.

1. Linear-chain mixed-valence nickel compound.
2. Shorter Ni-Ni distance in the dimer compared to the unoxidized one.
3. Nearly symmetrical Ni-I distances.
4. Equivalence of the Ni atoms from ESCA data.
5. Presence of an asymmetric broad absorption band in the near infrared region , at 6 kK.
6. Electrical conductivity at room temperature is $5 \times 10^{-6}\ \Omega^{-1}\,cm^{-1}$.
7. Semiconducting behaviour ,with low activation parameter $E_a \cong 0.07$ eV.

CONCLUSIONS.

A new linear-chain mixed-valence nickel compound has been prepared and characterized . The X-ray crystal structure consists of infinite chains of dimeric $[Ni_2S_8]$ units bridged by iodine atoms. The compound shows a semiconducting behaviour, $5 \times 10^{-6}\ \Omega^{-1}\,cm^{-1}$, with a small activation energy parameter $E_a = 0.07$ eV. The electrical conductivity can be explained by assuming a " hopping type " mechanism [7].

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