one, peaking at 0.26 T, in the low-field region. From the comparison with the spectra of $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$ and $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$, we assign the 0.36-T feature to the high-field component of g_{yy}, the low-field one being at 0.26 T. This yields, in approximate terms, $g_{yy} = 2.07$ and $D_{yy} = 317 \times 10^{-4}$ cm^{-1}. The bumps observed at fields lower than 0.26 T should correspond to the low-field transition of g_{zz}, the high-field one being in the region obscured by mononuclear copper impurities. The large signal between 0.26 and 0.32 T must be associated with g_{xx}. If this assignment is correct, and the similarity to the now well-characterized simple copper complexes makes this rather feasible, it seems that also in Cu_2Cu_2SOD, where the interacting metal ions are at least 600 pm apart, the zero-field splitting tensor still has relevant exchange contribution, since in the hypothesis of only dipolar terms D_{yy} could not exceed (60–70) $\times 10^{-4}$ cm^{-1}.

Acknowledgment. Thanks are due to Prof. S. J. Lippard for pointing out to us the misprint in ref 3.

Registry No. $[Cu(bpt)(CF_3SO_3)(H_2O)]_2$, 97150-35-1; $[(TMDT)_2Cu_2(im)(ClO_4)_2](ClO_4)$, 68829-54-9; Cu_2Cu_2SOD, 54651-53-5.

Contribution from the Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del CNR, Area della Ricerca di Roma, 00016 Monterotondo Stazione, Rome, Italy

Synthesis, X-ray Crystal Structure, and Chemical and Physical Properties of the New Linear-Chain Mixed-Valence Complex (μ-Iodo)tetrakis(dithioacetato)dinickel, $Ni_2(CH_3CS_2)_4I$, and X-ray Crystal Structure of the Precursor Tetrakis(dithioacetato)dinickel(II), $Ni_2(CH_3CS_2)_4$[†]

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Received August 28, 1984

The precursor tetrakis(dithioacetato)dinickel(II), $Ni_2(CH_3CS_2)_4$, crystallizes in the triclinic space group $P\bar{1}$ with the unit-cell dimensions $a = 9.017$ (3) Å, $b = 9.098$ (3) Å, $c = 11.272$ (4) Å, $\alpha = 105.07$ (2)°, $\beta = 67.67$ (2)°, and $\gamma = 93.44$ (2)°. The crystal structure of the complex consists of $[Ni_2S_8]$ dimeric units with a bridging acetate cage structure, in which the Ni–Ni distance is 2.564 (1) Å. The two $[NiS_4]$ squares are twisted 24° from the eclipsed geometry. Adjacent dimers in the unit cell are laterally displaced in such a way as to achieve a "slipped stack" arrangement, the nearest-neighbor contact being between sulfur and nickel. The iodine oxidative addition to the described compound gives a shining black crystalline product having the formula $Ni_2(CH_3CS_2)_4I$, where the formal oxidation number of the nickel atom is +2.5. This compound crystallizes in the monoclinic space group $P2/n$ with $a = 8.934$ (2) Å, $b = 8.382$ (2) Å, $c = 12.492$ (2) Å, and $\beta = 106.21°$. The crystal structure consists of linear chains of ---I---$[Ni_2S_8]$---I---$[Ni_2S_8]$--- stacking along the crystallographic b axis. The Ni–Ni distance in the dimer is 2.514 (3) Å, and the Ni–I distances are 2.928 (4) and 2.940 (4) Å, respectively. This is the first example, as far as we know, of a mixed-valence nickel compound, where linear chains of $[Ni_2S_8]$ chromophores, bridged through iodine, are present. The presence of a nearly symmetrical metal–iodine–metal bridge is responsible for the observed electrical conductivity, i.e. 5×10^{-6} Ω^{-1} cm^{-1}. Variable-temperature conductivity measurements show that the electrical conductivity follows an exponential temperature dependence, with an activation parameter, E_a, $\simeq$0.07 eV. A "hopping type" mechanism for the electrical conductivity is suggested.

Introduction

We recently found that several nickel-triad metal(II) derivatives of dithiocarboxylic acids, RCSSH, where R is an alkyl group, having columnar structure,[1,2] react with halogens.[3] In the case of the tetrakis(dithioacetato)diplatinum(II) complex,[2] two compounds were isolated. The first one, having the formula $Pt_2(CH_3CS_2)_4I_2$ with Pt formal oxidation state +3, is diamagnetic and consists of discrete $[Pt_2S_8I_2]$ units. The second one, having the formula $Pt_2(CH_3CS_2)_4I$, is a linear-chain mixed-valence compound, where the $[Pt_2S_8]$ units are linked by iodine atoms.[3] This compound belongs to the class of one-dimensional materials that has received considerable attention in the last few years,[4] and it is unusual because it is a semiconductor with a rather high maximum powder electrical conductivity, 7×10^{-3} Ω^{-1} cm^{-1}, at room temperature.[3,5]

With the aim of isolating new linear-chain compounds with sulfur donor ligands, we studied the reaction of the nickel and palladium analogues with halogens. Here we report the synthesis, the X-ray crystal structure, and the physical properties of the product obtained by reaction of tetrakis(dithioacetato)dinickel(II) with iodine and, for comparison, the X-ray crystal structure of the precursor tetrakis(dithioacetato)dinickel(II), $Ni_2(CH_3CS_2)_4$.

Experimental Section

Elemental analyses were performed by Alfred Bernhardt Mikroanalytische Laboratorium, Elbach, West Germany, and by Servizio Microanalisi del CNR, Area della Ricerca di Roma, Rome, Italy.

Reagents. Dithioacetic acid, CH_3CS_2H, was prepared according to known procedures.[6] $NiCl_2 \cdot 6H_2O$ was used as obtained from BDH Chemicals Ltd.

$Ni_2(CH_3CS_2)_4$. Tetrakis(dithioacetato)dinickel(II) was prepared as reported previously,[7] and the purity was checked by normal physicochemical methods. Crystals suitable for X-ray studies were grown by slow evaporation of a carbon disulfide solution of the complex. The RPE iodine was used as obtained commercially from Carlo Erba Ltd., without purification.

$Ni_2(CH_3CS_2)_4I$. $Ni_2(CH_3CS_2)_4$ (0.484 g, 1×10^{-3} mol) was dissolved in CS_2, 100 mL, and filtered, and a red-brown solution was obtained. Iodine (0.126 g, 5×10^{-4} mol) dissolved in the same solvent, 30 mL, was added dropwise to the red solution. A black, needlelike microcrystalline product immediately separated. Suitable crystals for X-ray investigations were obtained by the diffusion technique. Anal. Calcd for $C_8H_{12}S_8Ni_2I$ (M_r = 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.

[†] A preliminary communication of this work has been presented to the International Conference on the Physics and Chemistry of Low-dimensional Synthetic Metals, Abano Terme, Italy, June 17–22, 1984.

(1) Bellitto, C.; Flamini, A.; Piovesana, O.; Zanazzi, P. F. *Inorg. Chem.* **1980**, *19*, 3632.

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(4) (a) Kroogmann, K. *Angew Chem., Int. Ed. Engl.* **1969**, *8*, 35–42. (b) See for example: "Extended Linear-Chain Compounds"; Miller, J. S., Ed.; Plenum Press: New York, 1983; Vol. I–III.

(5) Che Chi-Ming; Herbstein, F. H.; Schaefer, W. P.; Marsch, R. E.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4604.

(6) Beiner, J. M.; Thuillier, A. *C. R. Seances Acad. Sci., Ser. C* **1972**, *274*, 642.

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Table I. Crystal Data and Experimental Conditions for the X-ray Intensity Measurements of $Ni_2(CH_3CS_2)_4$ (I) and $Ni_2(CH_3CS_2)_4I$ (II)

	$Ni_2(CH_3CS_2)_4$	$Ni_2(CH_3CS_2)_4I$
fw	482.08	609.02
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2/n$
cell parameters		
a, Å	9.017 (3)	8.934 (2)
b, Å	9.098 (3)	8.382 (2)
c, Å	11.272 (4)	12.492 (2)
α, deg	105.07 (2)	90.00
β, deg	67.67 (2)	106.21 (2)
γ, deg	93.44 (2)	90.00
Z	2	2
ρ_{calcd}, g cm^{-3}	1.94	2.25
ρ_{obsd}, g cm^{-3}	1.93 (2)	2.23 (2)
cryst dimens, mm	0.15 × 0.20 × 0.35	0.05 × 0.10 × 0.50
temp, °C	25	25
radiation	Mo Kα	Mo Kα
diffractometer	Syntex $P2_1$	Syntex $P2_1$
μ, cm^{-1}	37.60	46.56
monochromator	graphite cryst	graphite cryst
data collection	θ–2θ	θ–2θ
2θ range, deg	3.0–60.0	3.0–60.0
scan rate, deg/min	2.0–29.3	2.0–29.3
scan width, deg	(Mo Kα_1 – 2.0)–(Mo Kα_2 + 1.0)	(Mo Kα_1 – 1.0)–(Mo Kα_2 + 1.0)
total bkgd/scan time	0.5	0.5
no. of reflcns collected	7000	2829
no. of reflcns with $I > 3\sigma(I)$	3369	945
least-squares parameters	163	93
data/parameters ratio	20.7	10.2
final R	0.048	0.062
final R_w	0.057	0.069

Physical Measurements. Routine infrared spectra were recorded with a Perkin-Elmer 621 spectrophotometer on KBr pellets. The electronic spectra were recorded on a Cary 14 spectrophotometer. The compound was diluted in KBr and studied as KBr pellets.[8] A Beckman DK-2A was used to record diffuse-reflectance spectra on MgO-diluted samples. Differential scanning calorimetry, DSC, and thermal gravimetric analyses, TGA, were performed with a Stanton Redcroft STA-780 apparatus under N_2, scanning rate 5 °C/min. The static magnetic susceptibility, χ, was measured by the Faraday method, with the use of $Hg(Co(SCN)_4)$ as standard. EPR spectra were obtained with an X-band Varian E-9 instrument.

X-ray photoelectron spectra were recorded on a VG ESCA 3 MK II instrument using Al Kα (1486.6-eV) radiation, located at Servizio ESCA of the Area della Ricerca di Roma, CNR. As a check on the possible loss of iodine from $Ni_2(CH_3CS_2)_4I$ in the high-vacuum chamber of the spectrometer, the I $3d_{5/2}$ peak was recorded at the beginning and at the end of each run; no drop of intensity of this peak was observed. Samples were dusted on a double-sided adhesive tape. Binding energies reported are relative to the C 1s peak (285.0 eV) from the tape used as reference.

Electrical conductivity measurements were performed on polycrystalline samples and were obtained with the four-probe van der Paw method.[9] Samples were prepared by pressing powders under 7 kbar pressure into cylindrical pellets, 12 mm in diameter and typically 1 mm in thickness. The pellets were mounted on a boron nitride platelet with four fine gold wires, and electrical contacts were made with Du Pont silver paint. The current for dc conductivity measurements was supplied by a Keithley Model 225 regulated current source; voltage was measured on a Keithley Model 173 multimeter. Variable-temperature measurements were made by mounting the platelet on a Oxford Instruments modified CF 100 cryostat. The temperature was monitored with a CLTS sensor.

X-ray Structure Determination. Data for the two compounds were collected by following essentially the same procedure. Crystals of the two compounds suitable for X-ray investigation were obtained as described in the sample preparation section. Selected crystals were placed on a Nicolet $P2_1$ four-circle diffractometer. The cell dimensions were obtained by a least-squares refinement of setting angles of 15 automatic centered reflections ($2\theta > 25°$). A summary of main crystal data of both compounds and details of data collection are listed in Table I. Lorentz–polarization corrections, but no absorption corrections, were made. Preliminary diffraction photographs indicated triclinic symmetry for compound I, while the systematic absences were consistent with the monoclinic space group $P2/n$ for compound II (equivalent positions: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, \bar{y}, {}^1/_2 + z$; $^1/_2 - x, y, {}^1/_2 - z$). Both structures were solved by conventional Patterson and Fourier methods and refined by a full-matrix least-squares method using anisotropic temperature factors for non-hydrogen atoms. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with the weighting scheme $w = (\sin\theta)/\lambda$ for compound I and $w = 1.0/\sigma^2(F_o) + 0.1079F_o^2)$ for compound II. Residual, R, and weighted residual, R_w, indices were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and R_w

Table II. Atomic Fractional Coordinates for $Ni_2(CH_3CS_2)_4$

atom	x/a	y/b	z/c
Ni(1)	–0.05944 (9)	0.31930 (8)	0.37899 (7)
Ni(2)	0.0299 (9)	0.19954 (8)	0.12877 (7)
S(11)	–0.2485 (2)	0.1573 (2)	0.4331 (2)
S(21)	–0.2392 (2)	0.4773 (2)	0.3830 (2)
S(31)	0.1234 (2)	0.4913 (2)	0.3443 (2)
S(41)	0.1106 (2)	0.1715 (2)	0.3994 (2)
S(12)	–0.0504 (2)	–0.0249 (2)	0.1607 (2)
S(22)	–0.2056 (2)	0.2511 (2)	0.1276 (2)
S(32)	0.1184 (2)	0.4116 (2)	0.0718 (2)
S(42)	0.2733 (2)	0.1364 (2)	0.1073 (2)
C(1)	–0.1975 (7)	–0.0036 (6)	0.3108 (6)
C(2)	–0.2957 (7)	0.4007 (6)	0.2551 (6)
C(3)	0.1652 (8)	0.5225 (7)	0.1953 (7)
C(4)	0.2650 (7)	0.1188 (7)	0.2549 (7)
C(11)	–0.2896 (10)	–0.1422 (8)	0.3364 (9)
C(12)	–0.4422 (9)	0.4710 (9)	0.2532 (9)
C(13)	0.2561 (12)	0.6651 (10)	0.1707 (10)
C(14)	0.4115 (8)	0.0473 (14)	0.2561 (14)

Table III. Fractional Atomic Coordinates for $Ni_2(CH_3CS_2)_4I$

atom	x/a	y/b	z/c
Ni(1)	0.25	0.5971 (9)	0.25
Ni(2)	0.25	0.8970 (9)	0.25
I	0.25	0.2478 (8)	0.25
S(1)	0.4923 (4)	0.5836 (5)	0.3650 (3)
S(2)	0.1525 (4)	0.5850 (5)	0.3954 (3)
S(3)	0.5080 (4)	0.9141 (5)	0.2819 (3)
S(4)	0.2831 (4)	0.9113 (5)	0.4341 (3)
C(1)	0.5892 (14)	0.7483 (22)	0.3493 (10)
C(2)	0.7619 (6)	0.7478 (26)	0.4019 (12)
C(3)	0.2088 (14)	0.7498 (20)	0.4749 (9)
C(4)	0.1844 (20)	0.7463 (27)	0.5897 (11)

Table IV. Interatomic Distances (Å) and Selected Angles (deg), with Esd's in Parentheses, for $Ni_2(CH_3CS_2)_4$[a]

Ni(1)–Ni(2)	2.564 (1)	Ni(1)–S(31)	2.199 (2)
Ni(1)–S(11)	2.197 (2)	Ni(1)–S(31)^{I}	2.998 (2)
Ni(1)–S(21)	2.211 (2)	Ni(1)–S(41)	2.211 (2)
Ni(2)–S(12)	2.198 (2)	Ni(2)–S(32)	2.200 (2)
Ni(2)–S(22)	2.208 (2)	Ni(2)–S(42)	2.208 (2)
Ni(2)–S(12)^{II}	3.176 (2)		
S(11)–C(1)	1.674 (4)	S(32)–C(3)	1.674 (8)
S(21)–C(2)	1.678 (7)	S(42)–C(4)	1.686 (8)
S(31)–C(3)	1.672 (8)	C(1)–C(11)	1.50 (1)
S(41)–C(4)	1.665 (5)	C(2)–C(12)	1.51 (1)
S(12)–C(1)	1.678 (6)	C(3)–C(13)	1.52 (1)
S(22)–C(2)	1.675 (5)	C(41)–C(14)	1.51 (1)
S(11)–Ni(1)–S(21)	89.3 (1)	S(21)–Ni(1)–S(31)	90.4 (1)
S(11)–Ni(1)–S(41)	89.8 (1)	S(31)–Ni(1)–S(41)	89.9 (1)
S(12)–Ni(2)–S(22)	90.0 (1)	Ni(1)–S(11)–C(1)	107.8 (2)
S(12)–Ni(2)–S(42)	89.6 (1)	Ni(1)–S(21)–C(2)	108.2 (2)
S(22)–Ni(2)–S(32)	89.5 (1)	Ni(1)–S(31)–C(3)	110.1 (3)
S(32)–Ni(2)–S(42)	90.2 (1)	Ni(1)–S(41)–C(4)	108.9 (3)
Ni(2)–S(12)–C(1)	109.9 (2)	Ni(2)–S(32)–C(3)	107.1 (3)
Ni(2)–S(22)–C(2)	109.2 (3)	Ni(2)–S(42)–C(4)	108.4 (2)
S(11)–C(1)–S(12)	125.8 (4)	S(31)–C(3)–S(32)	126.2 (4)
S(21)–C(2)–S(22)	126.3 (4)	S(41)–C(4)–S(42)	126.3 (4)

[a] Symmetry code: (I) $\bar{x}, 1 - y, \bar{z}$. (II) $\bar{x}, \bar{y}, \bar{z}$.

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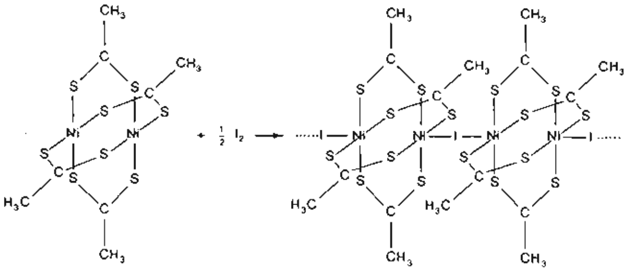
[8] Wrobleski, J. F.; Long, G. B. *J. Appl. Spectrosc.* **1977**, *31*, 177.

[9] Cahen, D.; Hahu, J. R.; Anderson, J. R. *Rev. Sci. Instrum.* **1973**, *44*, 1567.

Table V. Interatomic Distances (Å) and Selected Angles (deg), with Esd's in Parentheses, for $Ni_2(CH_3CS_2)_4I$

Ni(1)-Ni(2)	2.514 (5)	S(1)-C(1)	1.67 (2)
Ni(1)-I	2.928 (4)	S(2)-C(3)	1.69 (2)
Ni(2)-I	2.940 (4)	S(3)-C(1)	1.68 (2)
Ni(1)-S(1)	2.242 (3)	S(4)-C(3)	1.65 (2)
Ni(1)-S(2)	2.225 (3)	C(1)-C(2)	1.50 (2)
Ni(2)-S(3)	2.231 (4)	C(3)-C(4)	1.51 (2)
Ni(2)-S(4)	2.239 (3)		
S(1)-Ni(1)-S(2)	89.6 (1)	S(1)-C(1)-S(3)	125.2 (7)
S(3)-Ni(2)-S(4)	88.8 (1)	S(1)-C(1)-C(2)	117 (1)
Ni(1)-S(1)-C(1)	108.8 (5)	S(2)-C(3)-C(4)	124.6 (7)
Ni(1)-S(2)-C(3)	108.8 (5)	S(2)-C(3)-C(4)	116 (1)
Ni(2)-S(3)-C(1)	108.4 (6)	S(3)-C(1)-C(2)	118 (1)
Ni(2)-S(4)-C(3)	108.9 (5)	S(4)-C(3)-C(4)	119 (1)

Scheme I



a

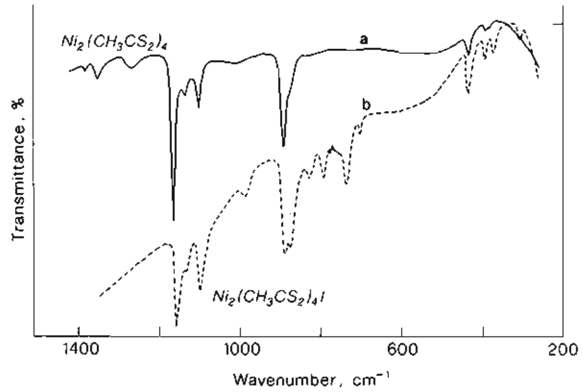


Figure 1. Infrared spectra (cm^{-1}) of $Ni_2(CH_3CS_2)_4$ and $Ni_2(CH_3CS_2)_4I$ in the KBr region.

$= |[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. The corresponding values converged to $R = 0.048$ ($R_w = 0.057$) for compound I and to $R = 0.062$ ($R_w = 0.069$) for compound II. Neutral scattering factors f' and f'' values, were used for all non-hydrogen atoms.[10] Computations for compound I were performed on the UNIVAC 1108 computer, located at the University of Rome,[11] and on the IBM 3330/168 CNUCE Computer, Pisa, Italy, by using the SHELX program system[12] for compound II. Final positional parameters for the two compounds are reported in Tables II and III and interatomic distances and angles in Tables IV and V.

Listings of observed and calculated structure factors and anisotropic thermal parameters for compounds I and II are available as supplementary material.

Results

The synthesis and chemical properties of the precursor $Ni_2(CH_3CS_2)_4$ compound have been reported previously.[7] The chemical oxidation of tetrakis(dithioacetato)dinickel(II) with iodine yielded a crystalline black needlelike product of formula a as reported in Scheme I. The nickel atoms are in the formal oxidation state +2.5. The compound has been characterized by elemental analysis, infrared spectra, and X-ray crystal structure (see below). The infrared spectrum of the oxidized material is similar to that found in the case of the platinum analogue[3] and is dominated by the presence of residual intensity (see Figure 1) due to the interband transition present in the near-infrared region with a maximum centered at 6×10^3 cm^{-1}. The compound is insoluble in polar solvents and slightly soluble in CS_2 ($<10^{-4}$ M), giving violet solutions. Differential thermal analysis, DSC, and thermogravimetric analysis, TGA, measurements show that the compound is stable up to 126 °C. At higher temperatures several not very well separated step losses are observed; the compound decomposes without melting.

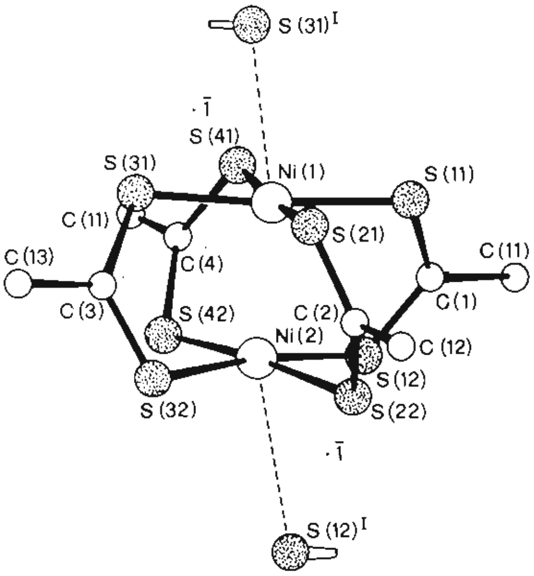


Figure 2. Atomic arrangement of $Ni_2(CH_3CS_2)_4$ showing Ni-S contact between adjacent molecules.

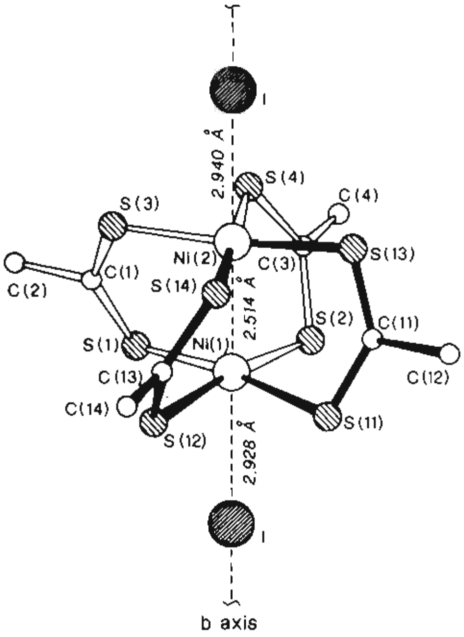


Figure 3. Atomic arrangement of $Ni_2(CH_3CS_2)_4I$ showing the Ni and I sequence along the *b* axis.

Description of the Crystal Structure of $Ni_2(CH_3CS_2)_4$. Structural information on $Ni_2(CH_3CS_2)_4$ is reported in Table IV and Figure 2. The crystal structure of tetrakis(dithioacetato)dinickel(II) consists of binuclear molecules involving four bridging ligands. Each nickel atom has five neighbors, i.e., four sulfur atoms and a nickel atom, in a tetragonally distorted square-pyramidal geometry. The Ni–Ni distance is 2.564 (1) Å, and the Ni–S

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(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(11) The set of crystallographic programs used on the UNIVAC computer have been developed by: Camether, B.; Spagna, R.; et al., Instituto di Strutturistica Chimica of the CNR, Area della Ricerca di Roma, unpublished work.

(12) Sheldrick, G. M.; "The SHELX program System; University Chemical Laboratory: Cambridge, U.K., 1976.

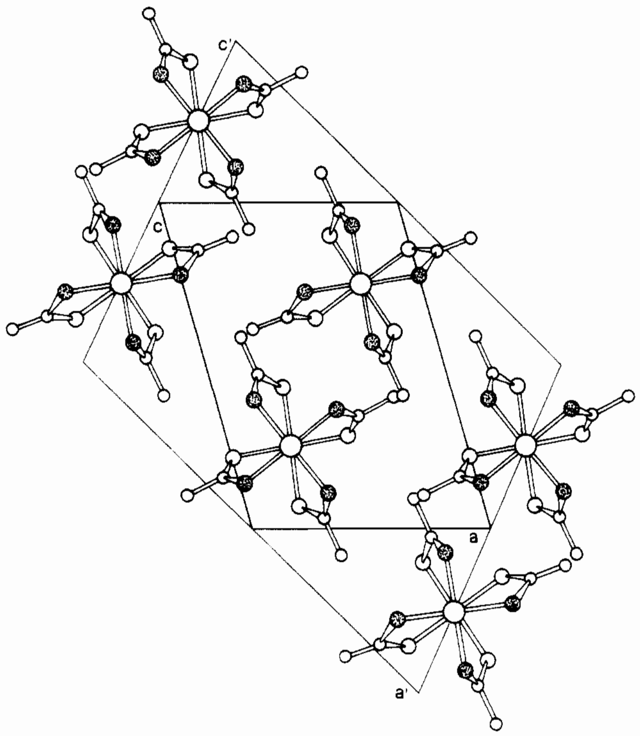

Figure 4. Atomic arrangement of $Ni_2(CH_3CS_2)_4I$ projected along the *b* axis.

distances range between 2.197 and 2.211 Å, similar to those found in the analogous tetrakis(benzenedithioacetato)dinickel(II),[13] i.e., 2.551 and 2.208–2.230 Å, respectively. Each nickel atom shows an "inward" displacement by 0.11 Å from the S_4 plane, in the direction of the other nickel atom. The two $[NiS_4]$ squares are twisted 24° from the eclipsed geometry. In the unit cell the dimeric units are in the "slipped-stack" arrangement so that there is a Ni–S contact between two adjacent molecules with $Ni(1)-S(31)^{I}$ = 2.998 (2) Å and $Ni(2)-S(12)^{II}$ = 3.176 (2) Å (see Table IV).

Description of the Crystal Structure of $Ni_2(CH_2CS_2)_4I$. Structural information on (μ-iodo)tetrakis(dithioacetato)dinickel is reported in Table V and Figures 3 and 4. The crystal structure consists of chains of $\cdots Ni_2(CH_3CS_2)_4\cdots I\cdots Ni_2(CH_3CS_2)_4\cdots$ lying along the twofold axes of the unit cell. As in the precursor compound the dimeric unit involves four bridging dithioacetate groups, each nickel being surrounded by four sulfur atoms in a square-planar arrangement. The two $[NiS_4]$ squares are twisted 28° from the eclipsed structure. The Ni–Ni distance in the dimer is 2.514 (3) Å, 0.23 Å shorter than the distance between the center of the S_4 squares. Ni–I distances are 2.928 (4) and 2.940 (4) Å, and all the nickel and iodine atoms lie on the twofold axes. A slightly shorter Ni–Ni distance, 2.514 Å, compared with that of the unoxidized compound, 2.564 Å, is observed, and this fact can be related to the change of the oxidation state of the metal. On the other hand, as has been observed the M–S distances change slightly compared with those of the unoxidized complex. This structure is similar to that found in $Pt_2(CH_3CS_2)_4I$.[3] The nickel compound is isostructural but not isomorphous with the platinum complex. A simple vectorial relationship between the unit cell dimensions of both compounds are found to be

$$a' = a - c \qquad b' \simeq b \qquad c' = a + c$$

where the apex refers to the platinum compound (see Figure 4).

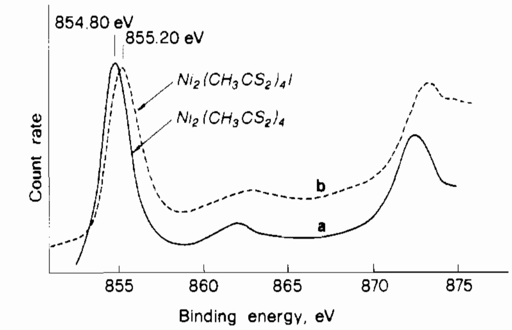

Figure 5. X-ray photoelectron spectra of $Ni_2(CH_3CS_2)_4$ (—) and $Ni_2(CH_3CS_2)_4I$ (- - -).

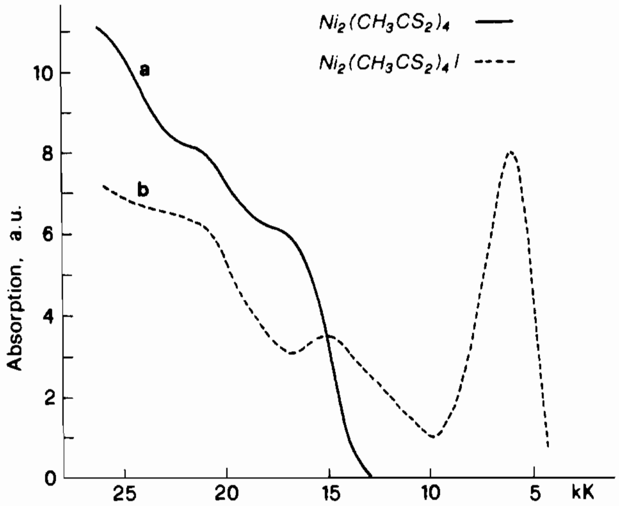

Figure 6. Diffuse-reflectance spectra of $Ni_2(CH_3CS_2)_4$ (—) and $Ni_2(CH_3CS_2)_4I$ (- - -).

Table VI. X-ray Photoelectron Spectroscopic Data for $Ni_2(CH_3CS_2)_4$ and $Ni_2(CH_3CS_2)_4I$[a]

material	Ni ($2p_{3/2}$)	S (2p)	halogen
$Ni_2(CH_3CS_2)_4$	854.80 (2.0)	162.70	
$Ni_2(CH_3CS_4)_4I$	855.20 (2.0)	162.60	619.10, 630.80

[a] Binding energies are in eV, with fwhm (full peak width at half-maximum) values in parentheses.

X-ray Photoelectron Spectra. X-ray photoelectron spectroscopy provides a powerful tool for clarifying the oxidation states of metal ions in compounds, especially in those containing two or more atoms of the same metal in different oxidation states such as mixed-valence compounds.[14] In the present case, the data gave the possibility of assessing the degree of fractional oxidation states and of the valence delocalization of the system.[15]

Figure 5 presents $2p_{3/2,1/2}$ spectra of $Ni_2(CH_3CS_2)_4$ and $Ni_2(CH_3CS_2)_4I$; data are listed in Table VI. The binding energies and line widths of both compounds are in good agreement with the literature for nickel compounds,[16] and they do not differ significantly except for a small energy shift. The full width at half-maximum (fwhm), 2 eV, is the same for both compounds, suggesting the presence of equivalent nickel atoms, on the XPS time scale ($\sim 10^{-18}$ s). The energy shift in the Ni $2p_{3/2}$ peak as one goes from the unoxidized to the oxidized species is significant, and the value is definitely less than that observed for Ni(II) and Ni(IV) (both for the same ligand[17]) and slightly less than for Ni(III) systems;[17,18] this is in agreement with the oxidation state of the oxidized compound. No shift is observed in the sulfur 2p peak, and this is a further evidence that the oxidation takes place only on the metal ion.[19] The XPS spectra are consistent with

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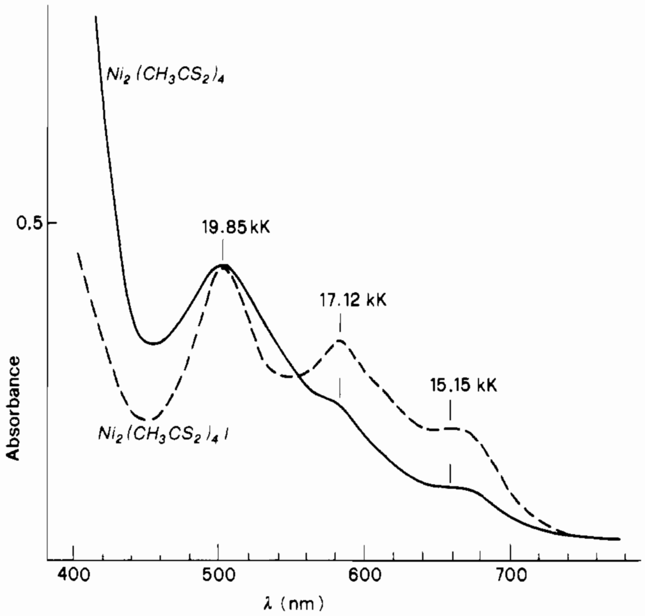

Figure 7. Solution spectra of $Ni_2(CH_3CS_2)_4$ (—) and $Ni_2(CH_3CS_2)_4I$ (---) both dissolved in CS_2 (see text).

a formulation involving a halogen-bridged Ni(II)–Ni(III) mixed-valence compound, having a linear-chain structure. Another remarkable feature is the absence of "shake up" satellites,[20] and this is in agreement with the observed diamagnetism of both compounds.

Electronic Spectra. Solid-state electronic spectra of both compounds are reported in Figure 6. The oxidation of $Ni_2(CH_3CS_2)_4$ introduces remarkable changes in the spectra. The most important one is the appearance in $Ni_2(CH_3CS_2)_4I$ of a strong asymmetric absorption band in the near-infrared region, with a maximum centered at 6×10^3 cm^{-1}, absent in the starting material. The band width at half-height, $\Delta\nu_{1/2}$, is 3000 cm^{-1}. $Ni_2(CH_3CS_2)_4I$ is almost insoluble in CS_2, and the absorption spectra of a very diluted solution, reported in Figure 7, is superposable on that of the starting material in the same solvent, suggesting the presence in solution of monomeric $Ni(CH_3CS_2)_2$ species. $Ni_2(CH_3CS_2)_4$, in fact, in solution dissociates to monomeric $Ni(CH_3CS_2)_4$,[7] and the optical spectrum is in accordance with those reported for complexes with $[NiS_4]$ chromophores.[21]

Magnetic Properties. (a) Magnetic Susceptibility Measurements. At room temperature $Ni_2(CH_3CS_2)_4I$ shows a negative value of the static magnetic susceptibility: $\chi_a = -7.00 \times 10^{-3}$ emu.

(b) Electron Spin Resonance. $Ni_2(CH_3CS_2)_4I$ is EPR silent. Very weak anisotropic signals are present, and they are thought to be due to impurities present in the compound.

Electrical Conductivity. At room temperature the electrical conductivity of several pellets of different samples of $Ni_2(CH_3CS_2)_4I$ ranged between 2×10^{-6} and 9×10^{-6} Ω^{-1} cm^{-1}. Variable-temperature studies of the electrical conductivity were carried out for several pellets, and thermally activated charge transport was observed. The apparent activation parameter, E_a, for three different samples was obtained by a least-squares fit to the usual equation

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

with E_a = 0.06–0.08 eV. This equation holds from 190 to 300 K.

Discussion

The oxidative addition of iodine to tetrakis(dithioacetato)dinickel(II) gives only one compound having the formula $Ni_2(CH_3CS_2)_4I$, where the formal oxidation state of the nickel is +2.5.

In comparison with the platinum dithioacetato analogues,[3] we were not able to isolate the single-valence complex $Ni_2(CH_3CS_2)_4I_2$, where the nickel atoms would be in the oxidation state +3.

The crystal structure of the title compound consists of infinite chains of ---I---$[Ni_2S_8]$---I---$[Ni_2S_8]$--- units. The molecular geometry of the dimeric unit is similar to that found in the precursor compound except for a small contraction in the Ni–Ni distance (0.05 Å). Each nickel atom is in an octahedral coordination, surrounded by four sulfur atoms and, in the axial positions, by the iodine and the other nickel. A remarkable feature is that the nickel–iodine distances along the chains are almost symmetric (i.e. 2.928 (4) and 2.940 (4) Å). The values are lower than that observed in Ni^{II} (diarsine)$_2I_2$, where the nickel(II) atoms are octahedrally coordinated,[22] i.e. 3.215 Å, and this is in agreement with the increase of the average oxidation number of the Ni. No comparison can be made with Ni(IV) and Ni(III) complexes with iodine as a donor atom, because as far as we know, no example with known structure has been reported to date. The structural results are in agreement with ESCA data, where only one type of nickel atom has been found.

The linear-chain compound can be then formulated as $[Ni_2(CH_3CS_2)_4I]_\infty$, with all the nickel ions equivalent.

The compound is a diamagnetic semiconductor with an intense broad absorption band at 6×10^3 cm^{-1}. The electronic and structural properties can be rationalized by using a model suggested by Hoffmann,[23] based on the extended Hückel method, and recently applied by Whangbo to Wollfram's red salt.[24]

Here, the chain can be viewed as being formed of $[Ni_2(CH_3CS_2)_4I_2]$ and $[Ni_2(CH_3CS_2)_4]$ units linked together along one direction, so that the Ni–I distances become nearly equal and the Ni atoms equivalent. The interaction can be considered to arise from Ni^{III} dimer and Ni^{II} dimer through the halogen bridge. Therefore, the two d_{z^2} bands in character are generated by a doubly occupied σ^* orbital in the Ni^{II} dimer and the corresponding empty σ^* orbital in the Ni^{III} dimer, with a small energy gap, E_g. The near-infrared region band arises from a transition between these two bands. The semiconducting behavior can also be explained on this basis. The electrical conduction may occur either by an intrinsic band mechanism or by a "hopping" mechanism. The former may be excluded because of the low apparent activation energy, 0.07 eV, which cannot be related to the near-infrared adsorption band, 0.75 eV. The latter mechanism seems the most appropriate for describing the electrical behavior for the following reasons:

(a) A similar behavior has been observed for the $M(NH_3)_2X_3$ compounds, where M = Pt, Pd and X = halogen.[25,26] For these compounds, it has been observed that the conductivity is enhanced with increase in the pressure and reaches a maximum value as the M(II)–X and M(IV)–X distances tend to become equal. The values of the conductivity and the activation energy at high pressure are comparable with those reported for the platinum derivative.[3]

(b) Comparison of the electrical conductivity of the title compound with that of $Pt_2(CH_3CS_2)_4I$ indicates that the conductivity decreases on going from Pt to Ni. This is in agreement with the degree of M–X orbital overlap which in the context of the "hopping" mechanism will influence the probability of the electron transfer via a tunneling process or the height of the activation energy barrier for the electron hopping.[27] This suggests that the nickel compound is less conductive than the platinum complex, as is observed.

(c) The activation parameter, E_a, is slightly larger in the Ni compound than in the Pt complex and should be related to the

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M–X stretching constant force.

From the data available we are not able to assess the contribution of the impurities to the conduction mechanism.

To summarize, this is the first reported example of this type of linear-chain nickel compounds.[28]

The only example where mixed-valence Ni ions are present is in the class of compounds having the formula $Li_xNi_{1-x}O$.[29] The higher oxidation state, Ni^{III} or Ni^{IV}, occurs in few compounds, all of them having coordination numbers of 5 or 6, and are present, in the solid state, as discrete molecules.[30,31]

Acknowledgment. This work has been financed by the Consiglio Nazionale delle Ricerche, Progetto Finalizzato "Chimica Fine e Secondaria". We wish to thank G. Cossu for ESCA measurements, M. Viola for drawings, and P. Filaci for technical assistance in magnetic measurements.

Registry No. $Ni_2(CH_3CS_2)_4$, 95974-45-1; $Ni_2(CH_3CS_2)_4I$, 95974-44-0; Ni, 7440-02-0; I_2, 7553-56-2.

Supplementary Material Available: Listings of all atomic coordinates and thermal parameters and of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Systematic Stereochemistry of Metal(II) Thiolates: Synthesis and Structures of $[M_2(SC_2H_5)_6]^{2-}$ (M = Mn(II), Ni(II), Zn(II), Cd(II))

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Received October 12, 1984

Heterogeneous reaction of a 3:1:1 mole ratio mixture of $NaSEt/MCl_2/Et_4NCl$ in acetonitrile affords the isomorphous compounds $(Et_4N)_2[M_2(SEt)_6]$, with the following crystal data given in the order M = Mn(II), Zn(II), Cd(II): $a = 10.993$ (1), 10.986 (2), 10.983 (4) Å; $b = 10.503$ (1), 10.436 (2), 10.525 (4) Å; $c = 18.306$ (2), 18.116 (4), 18.445 (7) Å; $\beta = 93.82$ (1), 118.70 (1), 94.56 (3)°; space group $P2_1/n$ and $Z = 2$ in all cases. Structures were solved by standard methods and refined to a conventional R value of ≤5.0%. The three $[M_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$ anions are edge-shared tetrahedra with imposed centrosymmetry and an anti conformation of bridging ethyl groups. A similar reaction mixture but containing Me_4NCl yielded $(Me_4N)_2[Ni_2(SEt)_6]$, for which $a = 10.775$ (2) Å, $b = 10.801$ (2) Å, $c = 16.891$ (4) Å, $\alpha = 104.03$ (2)°, $\beta = 95.05$ (2)°, and $\gamma = 58.81$ (1)°. The structure was refined to $R = 3.7\%$ in the triclinic space group $P\bar{1}$, revealing a centrosymmetric, nearly planar $[Ni_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$ anion formed by edge sharing of NiS_4 coordination units. From an analogous reaction system containing Et_4NCl, the trinuclear compound $(Et_4N)_2[Ni_3(SEt)_8]$ was isolated. The structure of $[Ni_3(\mu\text{-}SEt)_4(SEt)_4]^{2-}$ is briefly described. All known structures of metal(II) thiolates are summarized, and an empirical linear correlation between terminal and bridging ligand bond distances is presented. Coordination geometries tend to adhere closely to the normal stereochemical preference of M(II) ions. The dimensional flexibility of the $Ni_2(\mu\text{-}S)_2$ unit appears to be an important factor in its occurrence in four recognized structures, $[Ni_n(SR)_{2n+2}]^{2-}$ ($n = 2$, 3) and $Ni_n(SR)_{2n}$ ($n = 4$, 6).

Introduction

Our interest in the chemistry of discrete metal(II) thiolate complexes has arisen largely from their utility as precursors of metal–sulfide–thiolate clusters. In reactions with elemental sulfur the mononuclear tetrahedral complexes $[Fe(SR)_4]^{2-}$[1-4] yield one or more of the clusters $[Fe_2S_2(SR)_4]^{2-}$, $[Fe_3S_4(SR)_4]^{3-}$, $[Fe_4S_4(SR)_4]^{2-}$, and $[Fe_6S_9(SR)_2]^{4-}$, depending on the nature of the R group (Ph, alkyl) and experimental conditions.[1-3,5] The adamantane-like species $[Fe_4(SR)_{10}]^{2-}$,[1,6,7] with sulfur, affords $[Fe_4S_4(SR)_4]^{2-}$ in high yield.[1] The related cage complexes $[Fe_4(SPh)_6X_4]^{2-}$ (X = Cl, Br) can be formed from $[Fe(SPh)_4]^{2-}$ and $FeCl_2$ and, with dibenzyl trisulfide, produce $[Fe_4S_4(SPh)_2X_2]^{2-}$.[8] Further, $[Co_4(SPh)_{10}]^{2-}$[9] and hydrosulfide ion assemble the octanuclear cluster $[Co_8S_6(SPh)_8]^{4-}$,[10] and $[M_4(SPh)_{10}]^{2-}$[6,11,12] and sulfur yield the decanuclear cages $[M_{10}S_4(SPh)_{16}]^{4-}$ (M = Zn(II), Cd(II)).[13]

Stimulated by the earlier observations in this laboratory of the synthetic value of metal(II) thiolates,[1-3,10] we have undertaken a broader study of these compounds. The purpose of these investigations is to develop preparative routes to these compounds, thereby providing potential reactants leading to new clusters and cages, and to define structural types with the intention of evolving a systematic stereochemistry of metal(II) thiolate complexes. We have previously demonstrated that, with Fe(II), four types of species exist: $[Fe(SR)_4]^{2-}$, $[Fe_2(\mu\text{-}SR)_2(SR)_4]^{2-}$,[2,7] $[Fe_3(\mu\text{-}SR)_3Cl_6]^{3-}$,[2,14] and $[Fe_4(\mu\text{-}SR)_6(SR)_4]^{2-}$. In each, Fe(II) is tetrahedrally coordinated. Recent investigations of Mn(II),[15] Co(II),[7,9] and Cd(II)[12] systems, together with an earlier demonstration of a variety of $[M(SPh)_4]^{2-}$ complexes,[16] suggest that certain of these structural types may be of wide occurrence. The matter has been pursued here by the synthesis and structure determination of four complexes of the type $[M_2(SR)_6]^{2-}$, with M = Mn(II), Ni(II), Zn(II), and Cd(II). Also isolated in the course of this work was a trinuclear Ni(II) species of the type $[Ni_3(SR)_8]^{2-}$.

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