Preparation and properties of a metal dithiolene conductor, partially oxidized salt of tetra(n-butyl)ammonium bis(5,6-dithio-benzo[*d*]-1,3-dithiole-2-thione) nickelate, $(n\text{-}Bu_4N)_{0.29}[Ni(dmbit)_2]$

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Abstract

The title compound, the partially oxidized salt of tetra(n-butyl)ammonium bis(5,6-dithio-benzo[d]-1,3-dithiole-2-thione) nickelate (**11**), was crystallized electrochemically and its d.c. conductivity has been measured down to 10 K. It shows a metallic behavior from 300 to 220±20 K at which it has the maximum conductivity of 1.35±0.35 S/cm. Below 42 K it shows another metallic behavior again down to 20 K. The UV spectral evolution of ligand precursors caused by the incorporation of sulfur atoms has been discussed in relation to π-electron delocalization and conduction property. Cyclic voltammetry, IR and magnetic susceptibility have also been measured and discussed including the other related compounds.

Key words: Electric properties; Nickel complexes; Dithiolene complexes

Introduction

Solid state properties of bisdithiolene metal complexes with sulfur-enriched ligands have attracted much attention in the last decade because of their high electrical conductivity, and so far five compounds [1, 2] were found to be molecular superconductors all of which are based upon the metal dmit complex (dmit = 4,5-dimercapto-1,3-dithiole-2-thione). As an extension of π-conjugation of the dmit moiety, Larsen and Bechgaard [3] and Coustumer *et al.* [4] have reported a preliminary conduction study on the dmbit complex where a benzene ring is incorporated into the dmbit moiety (dmbit = 5,6-dithio-benzo[*d*]-1,3-dithiole-2-thione). We have examined the dmbit complex in more detail and the title compound was crystallized in a conglomerate form. Its four probe conductivity was measured down to 10 K. Here, the conduction property, UV and IR spectra, cyclic voltammetry (CV) and magnetic susceptibility of Nidmbit complex are reported. Preliminary results have already been reported [5].

Experimental

Syntheses

The ligand precursors and metal bisdithiolene complexes were prepared according to the literature methods [6, 7] as is illustrated in Scheme 1. All solvents used were dried over a powder type molecular sieve (4 Å), and de-oxygenated by argon bubbling before each reaction. All reactions involving sodium metal were carried out under argon atmosphere.

Preparation of $(n\text{-}Bu_4N)_{0.29}[Ni(dmbit)_2]$ (11)

Chemical oxidation. The monovalent salt of tetra(n-butyl) ammonium, Nidmbit (**10**) was dissolved in acetonitrile and oxidized with a 0.1 mol/l ethanol solution of bromine or with $n\text{-}Bu_4NBr_3$ in acetone. The black precipitate was separated by filtration and washed with acetonitrile or ethanol and dried *in vacuo*.

Galvanostatic oxidation. Crystals of the partially oxidized salt of $Ni(dmbit)_2$ were obtained by a galvanostatic electrolysis of a 1,2-dichloroethane solution containing $n\text{-}Bu_4N[Ni(dmbit)_2]$ (**10**) and ~0.02 mol/l of $n\text{-}Bu_4NClO_4$ as an electrolyte. An H-shaped cell where

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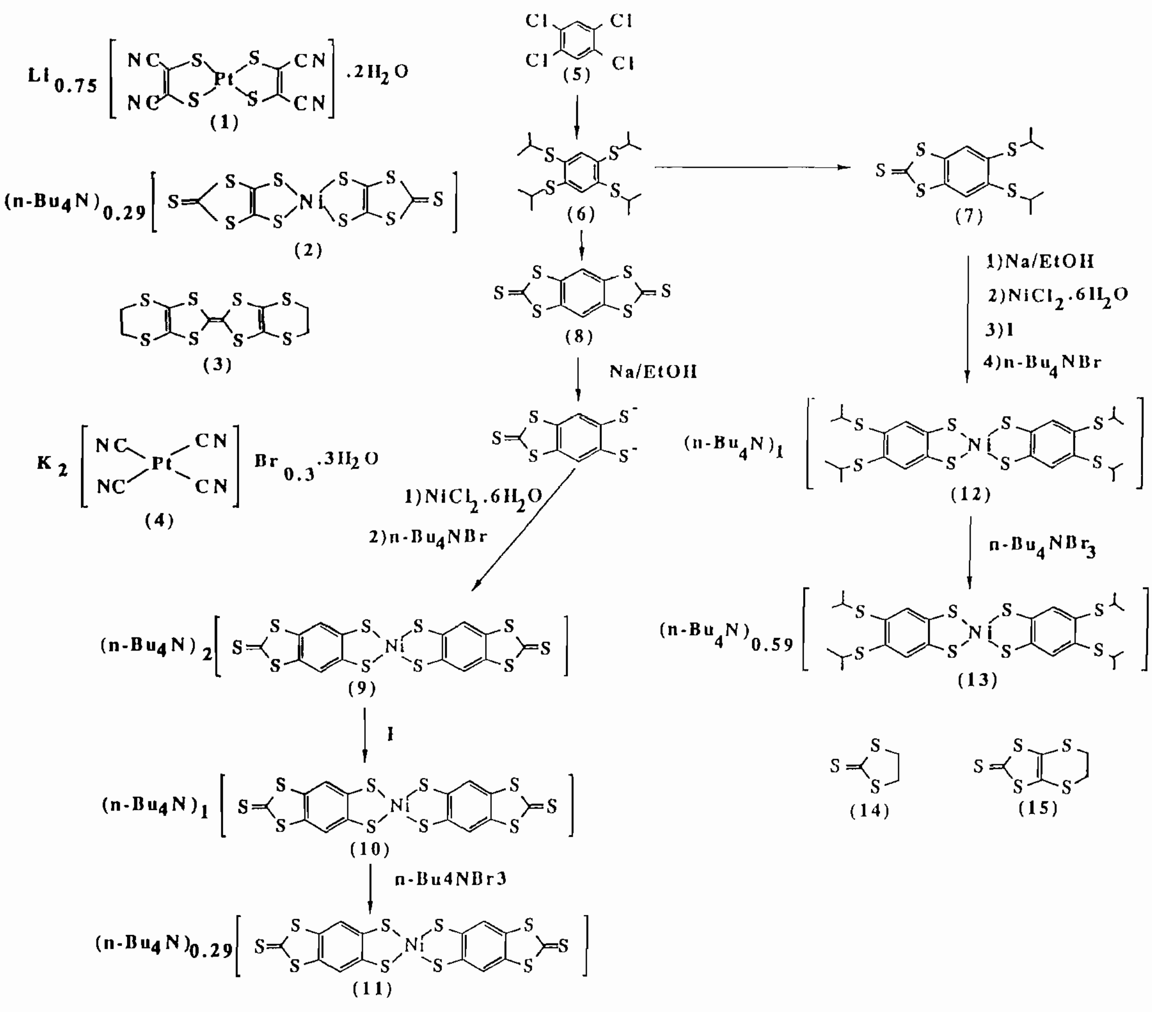

Scheme 1.

the anode and cathode are separated by a medium porosity glass frit was used with platinum electrodes of 1 mm diameter. The current was held constant at 2 μA. Within one week black dendrite-like crystals were formed on the anode. They were collected by filtration, washed with 1,2-dichloroethane and dried in air.

Crystals are irregular shaped with typical dimensions of (5–7) × (0.2–0.4) × (0.2–0.4) mm, seemingly conglomerates of microcrystals. It is also possible to use a divalent salt **9** instead of the monovalent one **10** as the starting compound to obtain the partially oxidized species. But, the divalent salt of Nidmbit is less soluble in 1,2-dichloroethane than the monovalent one and only a tiny block of crystals was obtained when the divalent salt was used.

Elemental analysis confirmed the molecular formula of the partially oxidized salt **11** as $(n\text{-}Bu_4N)_{0.29}[Ni(dmbit)_2]$, the cation deficiency of which coincides with the corresponding salt of the $Ni(dmit)_2$ complex as reported by Valade *et al.* [8], while Larsen and Bechgaard reported a different formula, $(n\text{-}Bu_4N)_{0.198}[Ni(dmbit)_2]$ for their electrochemically oxidized sample [3]. IR (KBr, cm^{-1}): $\nu = 1454$ (C=C), 1053 (C=S), 451 (Ni–S). *Anal.* Calc.: C, 36.00; H, 2.34; N, 0.65. Found: C, 36.14; H, 2.37; N, 0.63%.

The syntheses of the other related complexes are as follows.

Bis(5,6-dithio-benzo[d]-1,3-dithiole-2-thione) nickelate tetra(n-butyl)ammonium divalent salt (9)

In a dry three-necked and round-bottomed 300 ml flask fitted with a condenser and gas inlet, 200 ml of dry ethanol are placed and 0.5 g of dithione is suspended with magnetic stirring. 2 g of sodium metal is added to the suspension and heated to reflux under Ar flushing for 1 h. After all the sodium metal has dissolved, 0.205 g of $NiCl_2 \cdot 6H_2O$ in a small amount of water is added. A dark brown precipitate is immediately formed. After several minutes of agitation, 0.556 g of $n\text{-}Bu_4NBr$ in ethanol is added followed by 30 min of stirring and the product is separated by filtration, washed with water and dried *in vacuo*; m.p. 154–155 °C. UV ($CHCl_3$, nm): $\lambda = 262.5$(s), 314.0(s), 395.0(s), 570.0(m), 950.0(w). IR (KBr, cm^{-1}): $\nu = 1453$ (C=C), 1048, 1024 (C=S), 422 (Ni–S). *Anal.* Calc.: C, 53.31; H, 7.39; N, 2.70; S, 30.94. Found: C, 53.28; H, 7.70; N, 2.87; S, 30.90%.

Bis(5,6-dithio-benzo[d]-1,3-dithiole-2-thione) nickelate tetra(n-butyl)ammonium monovalent salt (10)

0.97 g of $(n\text{-}Bu_4N)_2Ni(dmbit)_2$ (**9**) was completely dissolved in ~80 ml of warm dimethyl formamide (DMF). 0.226 g of $n\text{-}Bu_4NBr_3$ in 10 ml of DMF was added to the solution under agitation. Then ~50 ml of ethanol and 50 ml of acetonitrile were added and the solution was cooled to ice temperature in a refrigerator for several days. Black needle crystals were separated, washed with ethanol and stored *in vacuo*; m.p. 227–229 °C. UV ($CHCl_3$, nm): $\lambda = 263.0$(s), 315.5(s), 373.0(s), 407.5(s), 446.5(m), 556.5(w), 948.5(s). IR (KBr, cm^{-1}): $\nu = 1458$ (C=C), 1055 (C=S), 435 (Ni–S). *Anal.* Calc.: C, 45.38; H, 5.09; N, 1.76; S, 40.38; Ni, 7.39. Found: C, 45.31; H, 5.06; N, 1.86; S, 40 17; Ni, 7.60%.

Bis(1,2-di(isopropylthio)benzene-4,5-dithiole) nickelate tetra(n-butyl)ammonium monovalent salt (12)

The monovalent Nidmbbip complex salt, $(n\text{-}Bu_4N)[Ni(dmbbip)_2]$ (**12**), was prepared using 1 g (3 mmol) of **3** and 0.14 g (6 mmol) of Na metal dissolved in 60 ml of absolute ethanol. The reaction mixture was refluxed for 3 h to open the isotrithione ring. After cooling it down to room temperature, $NiCl_2 \cdot 6H_2O$ (0.36 g, 1 5 mmol), $n\text{-}Bu_4NBr$ (0.97 g, 3 mmol) and iodine (0.19 g, 0.75 mmol) were added successively as shown in Scheme 1. The product is not crystalline but a black tarry substance. UV ($CHCl_3$, cm^{-1}). $\lambda = 268.5$(s), 314.0(s), 381.0(sh), 982.0(w). IR (KBr, cm^{-1}): $\nu = 1453$ (C=C), 1044, 1019 (C=S), 876, 846 (δCH, out of plane), 416 (Ni–S). *Anal.* Calc.: C, 54.71; H, 7.08; N, 1.59; S, 29.21. Found: C, 54.37; H, 8.00; N, 2.15; S, 29.28%.

Bis(1,2-di(isopropylthio)benzene-4,5-dithiole) nickelate tetra(n-butyl)ammonium partially oxidised salt, $(n\text{-}Bu_4N)_{0\,59}[Ni(dmbbip)_2]$ (13)

0.38 g of $(n\text{-}Bu_4N)[Ni(dmbbip))_2]$ (**12**) is dissolved in 30 ml of acetonitrile and 0.03 g of $n\text{-}Bu_4NBr_3$ in 5 ml of acetonitrile is added with agitation. After 1 h the black precipitate is separated by filtration and washed with acetonitrile and methanol. UV ($CHCl_3$, nm): $\lambda = 276.0$(s), 315.0(s), 983.5(m). *Anal.* Calc.: C, 51.57; H, 6.89; N, 1.06; S, 32.94. Found: C, 51.27; H, 7.20; N, 1.06; S, 32.96%.

Physical measurements

Conductivity measurements

Four-probe conductivity measurements were carried out using a Keithley model 220 current source, model 169 voltmeter and model 705 scanner controlled by an NEC 9801F personal computer. Using colloidal graphite the crystals were glued on four gold wires of 25 μm diameter which were soldered to the pin hole of a DIP socket with 8 pins. The mounted crystals were placed in an Osaka Sanso Cryo-mini-D refrigerator with helium gas circulation for the variable temperature measurements using an Oxford ITC4 temperature controller. Measurements on four different samples from two different batches were performed and gave reproducible results.

Two-probe conductivity measurements were also carried out on the powder samples in the state of pressed pellets of 3 mm diameter under ~7 t/cm^2 using a Keithley model 614 electrometer at room temperature.

Other physical measurements

Most of the elemental analyses were performed at the RIKEN Institute and partly performed at the National Institute of Materials and Chemical Research. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded by an Hitachi R-40 high resolution NMR spectrophotometer (90 MHz) using TMS as the internal reference in $CDCl_3$. Mass spectra were obtained by a Hewlett Packard 5995A GC/MS spectrometer with a 9825 computer system. IR spectroscopic measurements were performed with a Jasco A302 diffraction grating spectrophotometer using KCl or KBr pellets over the range 5040–330 cm^{-1}. Magnetic susceptibility data were collected on a polycrystalline sample in an inert atmosphere with a Faraday type magnetobalance from 77 to 300 K. The diamagnetic corrections were estimated according to Pascal constants and constitutive corrections.

Cyclic voltammetry measurements for the nickel complexes were carried out in acetonitrile of liquid-chromato grade with 0.1 mol/l $n\text{-}Bu_4NClO_4$ as supporting electrolyte using $Ag/AgNO_3$ as reference electrode, which was calibrated with ferrocene. For the potentiostat and function generators Hokuto Denko model HA-501 and model HB-104 were used, respectively.

Results and discussion

The precursor 1,3,5,7-tetrathia-s-indacene-2,6-dithione (**8**) was found to be a more versatile synthon than the dione analogue [3] of **8** for the preparation of various new potentially conductive metal complexes with extended π-electronic conjugation on the planar ligands. Although the decreasing solubility of these materials makes it more tedious to identify and purify them than for dmit complexes (**2**), they can help in understanding the role of electronic conjugation in the conduction property as well as more new conductive complexes.

The partially oxidized species $(n\text{-}Bu_4N)_{0.29}[Ni(dmbit)_2]$ (**11**) is obtained either by chemical oxidation or galvanostatic oxidation. Both methods gave the same analytical results within experimental error. However, due to the sparing solubility in the common organic solvents, only a black powder was obtained through the chemical oxidation by Br_2 or $n\text{-}Bu_4NBr_3$. No crystals were obtained by the attempted slow diffusional crystal growth using $n\text{-}Bu_4NBr_3$ and $(n\text{-}Bu_4N)[Ni(dmbit)_2]$ (**10**) in acetonitrile. Electrochemical crystallization using galvanostatic oxidation in a 1,2-dichloromethane solution of $(n\text{-}Bu_4N)[Ni(dmbit)_2]$ (**10**) gave irregular shaped black bars which are long and strong enough for the conduction study. When acetonitrile was used as the solvent for galvanostatic oxidation it only gave small conglomerates of the micro crystals on the anode. Single crystal growth is desirable for conduction and structural studies, but in spite of our long-term efforts we have not yet been successful.

Electrical conductivity of $(n\text{-}Bu_4N)_{0.29}[Ni(dmbit)_2]$

A pressed pellet sample of the partially oxidized n-butyl ammonium salt has a conductivity value in the range $(1\text{–}2.1)\times10^{-2}$ S/cm at r.t. Four-probe measurement on the four crystals grown electrochemically shows an average conductivity of 1.08 ± 0.34 S/cm at room temperature, which is 100 times higher than the value of the pressed pellet sample and falls in the same order of magnitude as that of the corresponding dmit single crystals, $(n\text{-}Bu_4N)_{0.29}[Ni(dmit)_2]$ (**2**) (1–10 S/cm). Coustumer *et al.* [4] reported a conductivity value measured on pressed pellets of 0.2 S/cm for their non-stoichiometric oxidation product $(n\text{-}Bu_4N)_{0.30}[Ni(dmbit)_2]$.

The temperature dependency of the d.c. conductivity for one of the examined four samples is illustrated in Fig. 1. The general behavior is as follows. The conductivity goes up with decreasing temperature from 300 down to 252–190 K (220 ± 20 K), at which temperature it has the averaged maximum value of 1.35 ± 0.35 S/cm. Below this temperature it decreases with decreasing temperature down to 45–42 K. However, below this temperature it again goes up until it reaches another maximum of 0.24 ± 0.09 S/cm at 22 K and then rests.

When the temperature is increased, the conductivity follows a similar path back to the room temperature value showing a hysteresis to some extent. All the examined samples showed the same behavior. After the metallic-like behavior around r.t. it passes through a gradual metal–semiconductor transition. This is very similar to the one observed for $K_2[Pt(CN)_4]Br_{0.3}\cdot3H_2O$ (**4**), $Li_{0.75}[Pt(mnt)_2]\cdot2H_2O$ (**1**) and other one-dimensional platinum chain complexes [9]. Another metallic-like behavior which appeared around 40 K is very unusual and of great interest. The closest prototype metal dithiolene, $(n\text{-}Bu_4N)_{0.29}[Ni(dmit)_2]$ (**2**), has the same cation stoichiometry as that of the corresponding $Ni(dmbit)_2$ salt but it behaves as a semiconductor down to 30 K and has no metallic-like behavior region. This conduction behavior at low temperature could be induced by a structural phase transition but it also seems similar to the reentrant behavior found for DCNQI complexes [10] under enhanced pressure. A more similar conductivity behavior was reported for the trimethylammonium salt of Ni dmit complex [11] at 10 K, but it was denied later by one of the authors as an incorrect report at ICSM '92.

Cyclic voltammetry

The CV results for $(n\text{-}Bu_4N)[Ni(dmbit)_2]$ (**10**) show two sets of redox potential peaks. The lower set of potential peaks is centered at -311 mV and is assigned to the one-electron reversible redox process between dianion and monoanion species. The higher set of potential peaks is centered at 48 mV and corresponds to the irreversible reaction between the monoanion and the neutral complexes. The potential difference between the two successive one-electron transfer reactions of this complex ($\Delta E_{1/2}=359$ mV) is smaller than the reported one (560 mV) [3] and is comparable to that of $(Et_4N)[Ni(dmit)_2]$ (297 mV).

Magnetic susceptibility

The temperature dependence of the magnetic susceptibility for $[Ni(dmbit)_2]^{1-}$ (**10**) has been measured over the temperature range between 77 and 300 K. The plot of the inverse molar magnetic susceptibility versus temperature after diamagnetic correction shows a typical feature of behavior following the Curie-Weiss law; $\chi_M=C_M/(T-\theta)$ where C_M is the molar Curie constant in emu K/mol and θ the Weiss constant in Kelvin. The temperature independent part χ_{TIP} is obtained as $\chi=\chi_{TIP}+C_M/(T-\theta)$ with $\chi_{TIP}=(8.02\pm0.44)\times10^{-4}$ emu/mol within the low-temperature range ($80<T<100$ K). This value of χ_{TIP} is comparable to or bigger than the reported value for other Ni^{2+}(d^8) ions. The results after computer fit correspond to the parameter values: $C_M=0.38$ emu K/mol and $\theta=-5.94$ K as illustrated in Fig. 2. The negative sign of the Weiss constant indicates an antiferromagnetic interaction between the neighboring nickel ions in the applied temperature range, but its magnitude is very small. The effective magnetic moment is 1.74 BM, which is derived from the relation

$$\mu_{eff}=(3k/N\beta^2)^{1/2}\sqrt{\chi_M(T-\theta)}$$

where k is Boltzmann's constant, N Avogadro's number and β the Bohr magneton. These magnetic moments are very close to the spin-only value ($\mu_{so}=1.73$ BM) of low-spin species Ni^{3+} (d^7, $S=1/2$) and Ni^{1+} (d^9,

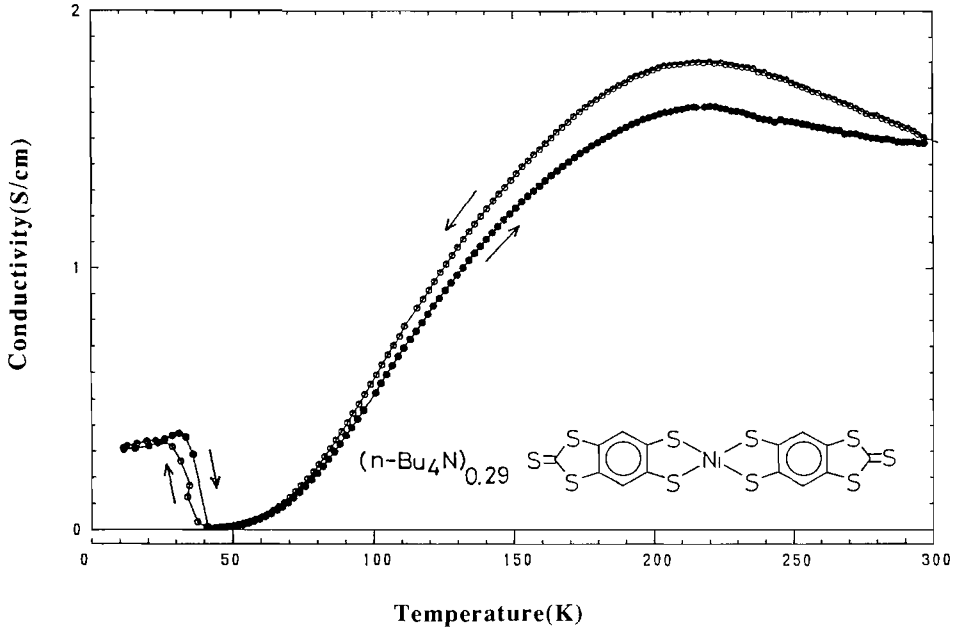

Fig 1 Temperature dependence of conductivity along the elongated direction for a polycrystalline conglomerate of (n-Bu$_4$N)$_{0.29}$[Ni(dmbit)$_2$] (**11**). Inserted arrows indicate the direction of the thermal process

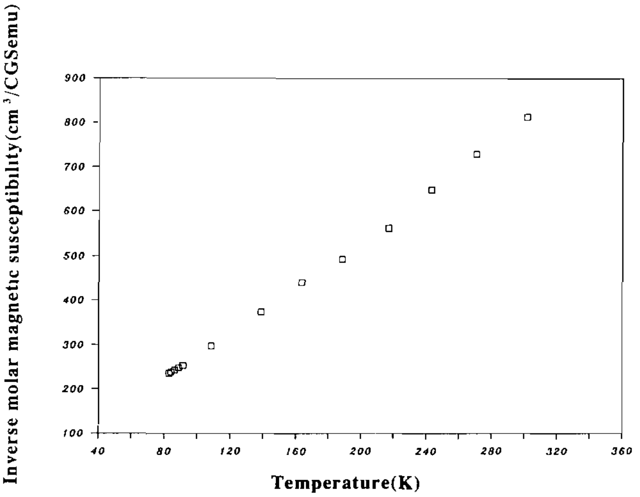

Fig. 2 Temperature dependence of the inverse molar magnetic susceptibility for (n-Bu$_4$N)[Ni(dmbit)$_2$] (**10**) (μ_{eff} = 1.74 BM, C_M = 0.38 emu/mol, μ_{so} = 1.73 BM, θ = −5.9 K).

$S = 1/2$). These results could also be consistent with the d^8 state (Ni^{2+}, $S = 0$) if one electron on the ligand is partially delocalized into the central nickel ion to make $[Ni^{2+}(dmbit)_2]^{1-}$ rather than $[Ni^{3+}(dmbit)_2]^{1-}$, as pointed out by Schultz *et al.* [12] on the (n-Bu$_4$N)[Ni(dddt)$_2$] complex (dddt: 5,6-dihydro-1,4-dithiin-2,3-dithiolate). The nickel ion is known to stay mostly as diamagnetic Ni^{2+} when coordinated to a sulfur atom. The dmbit ligand has a π-electron conjugation system and the electron tends to delocalize in the ligands. The magnetic moment close to the spin-only value seems to suggest that as a whole complex anion the spin resides mainly on the ligand. For more reliable information about the oxidation state of the central metal atom, ESR measurements of the *g* value would be decisive.

UV spectral evolution

One of the key aspects of the electronic structure of the ligand for the conductive metal complexes seems to be in the intermediate π-electronic conjugation via sulfide bridges, which is common to the both BEDT-TTF (bis-ethylenedithio-tetrathiafulvalene; the most potential donor for organic superconductors) and metal dmit complexes. The spectral evolution during the synthesis of the dmbit complex is as follows.

As shown in Fig. 3, tetrakis(isopropylthio)benzene (**6**) has a similar profile to mercaptobenzene C_6H_5–SH. Upon the introduction of one or two thiocarbonyl(s) into **6** to form 5,6-di(isopropylthio)benzo[*d*]-1,3-dithiole-2-thione (**7**) or 1,3,5,7-tetrathia-s-indacene-2,6-dithione (**8**), respectively, a strong and symmetric absorption band appears at 386.0 or 391.5 nm, respectively, which is assigned to the characteristic absorption band due to the thiocarbonyl. Conjugation between the thiocarbonyls and benzene ring through the sulfide bridges is noticed by taking into account the much lower peak position at 318 nm of the isolated thiocarbonyl bond in ethylenetrithio-carbonate (**14**). Concerning the conjugation in (2,5,7,9-tetrathia bicyclo[4.3.0]non-1(6)-en-8-thione) (**15**), the thiocarbonyl band at 409.0 nm blue-shifts to 386.0 nm upon replacement of the ethylene

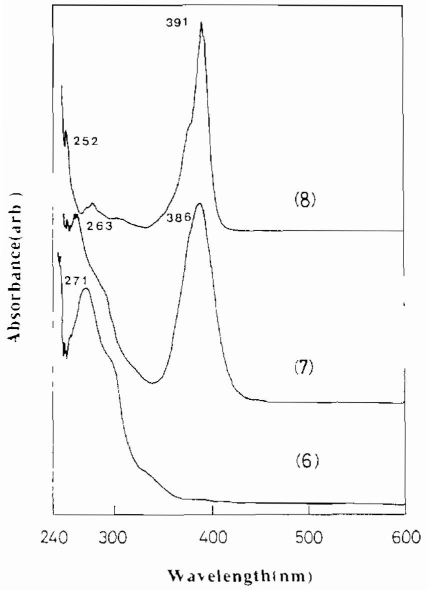

Fig 3 UV spectra of the ligand precursors: tetrakis-(isopropylthio)benzene (**6**), 5,6-bis(isopropylthio)benzo[*d*]-1,3-dithiole-2-thione (**7**), 1,3,5,7-tetrathia-s-indacene-2,6-dithione (**8**) (with 10 mm path length in chloroform)

skeleton with the benzene ring suggesting the dmbit ligand has a less conjugative structure than dmit.

Thus the size of the π-electronic system becomes larger in dmbit but the extent of conjugation is slightly diminished between the end thiocarbonyl and inner double bond groups. This picture may help us to understand why dmbit complexes have a slightly bigger on-site Coulomb repulsion energy and lower electrical conductivity than the corresponding dmit complexes.

Tetra(n-butyl)ammonium salts of the dianionic complex $(n\text{-}Bu_4N)_2[Ni(dmbit)_2]$ (**9**) show an absorption spectra where one new strong band and another two weak bands appear, Fig. 4, which are assigned to the intra-complex transition between the ligands and nickel ion. In the monoanion salt **10**, more new bands emerge and the lowest-lying weak band at 950 nm is enhanced to a strong band while the second lowest-lying band is weakened.

The partially oxidized salt **11** is sparingly soluble in the common organic solvents and no reliable solution spectra were obtained. However, an attempted preparation of a solid thin film was successful using electrochemical deposition on an indium-tin-oxide-coated quartz glass. The solid spectra of the partially oxidized species have a broad and strong peak with a shoulder in the short wavelength region and a very weak hump in the intra-complex charge transfer region.

IR spectra

IR spectral data of these salts are summarized in Table 1 During the oxidation process of the complex

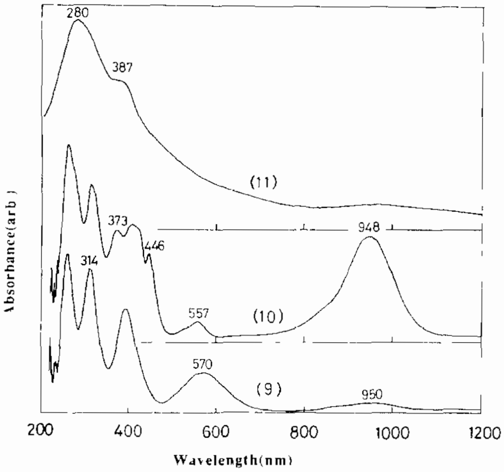

Fig. 4 UV spectra of the tetra(n-butyl)ammonium salts of $Ni(dmbit)_2$ divalent **9** and monovalent **10** (with 10 mm path length in chloroform) and partially oxidized salt **11** (electrochemically deposited on ITO coated quartz plate)

TABLE 1 Vibrational frequencies (cm^{-1}) of Nidmbit complexes KBr pellets, s. strong, m medium, w weak

Compound	Charge	ν(C=C)	ν(C=S)	ν(Ni–S)
9	−2	1453m	1048s, 1024m	422m
10	−1	1458m	1055s, 1025w	435m
11	−0 29	1454m	1053s	451w

salt, C=C and C=S stretching vibrational frequencies stay almost constant contrary to the expected sensitivity to the oxidation state. Valade *et al.* suggested that the Ni–S frequency increase is more consistent with the decrease of the Ni–S bond length [8]. An increase of the Ni–S vibrational frequency is observed here also, see Table 1. These structural and spectroscopic results reveal that the central metal ion is more involved in the oxidation process than the ligands.

In relation to the optical property of the Nidmbit complex, it is noteworthy that $(n\text{-}Bu_4N)[Ni(dmbit)_2]$ (**10**) was recently found to have a relatively high third-order optical non-linearity ($\chi(3) = 3.6 \times 10^{-11}$ esu by the THG Maker fringe method) [13].

Physical properties of other related complexes

Single crystals of $(n\text{-}Bu_4N)[Ni(dmbit)_2]$ (**10**) of good quality were obtained by recrystallization from DMF/ethanol/acetonitrile. The four-probe conductivity of a single crystal along the elongated axis (*c* axis) was 6×10^{-7} S/cm at r.t. This means the conductivity of the complex salt is enhanced by a factor of 10^6–10^7 when the monovalent salt is partially oxidized. Only a powder sample has been obtained so far for the $(n\text{-}Bu_4N)_{0\ 59}[Ni(dmbbip)_2]$ (**13**) complex salt and its pressed pellet conductivity was $(0.5\text{–}6.5) \times 10^{-7}$ S/cm at r.t. In the moiety of dmbbip there is no thiocarbonyl group bonded to the 1,2,4,5-tetrathio-benzene, which has a reduced π-electron delocalization over the complex anion leading to the very low conductivity even if it is partially oxidized.

The lattice constants of a single crystal of (n-Bu_4N)[Ni(dmbit)$_2$] (**10**) were determined using an Enraf-Nonius CAD4 diffractometer. Crystal data; $M = 793.96$, triclinic, $a = 15.152(4)$, $b = 15.313(4)$, $c = 16.702(4)$ Å, $\alpha = 83.78(2)$, $\beta = 85.77(2)$, $\gamma = 71.66(2)°$, $V = 3646.8$ Å^3, $Z = 4$, $D_m = 1.43$ g/cm^3, $D_c = 1.44$ g/cm^3.

The CV prediction for the Nidmbbip (**12**) complex is a larger value (780 mV) than any others, so it is expected that this complex will have the lowest conductivity of all. Actually, the measured conductivities for the pressed pellets are 10^{-11} S/cm for (n-Bu_4N)[Ni(dmbbip)$_2$], 10^{-9} S/cm for (n-Bu_4N)[Ni(dmbit)$_2$] and 10^{-7} S/cm for (Et_4N)[Ni(dmit)$_2$] in agreement with the order of the CV prediction.

The temperature dependence of the magnetic susceptibility for [Ni(dmbbip)$_2$]$^{1-}$ (**12**) was measured over the temperature range between 77 and 300 K. The plot of the inverse susceptibility versus temperature after diamagnetic correction shows a typical feature of behavior following the Curie-Weiss law. The results correspond to the parameter values: $C_M = 0.39$ emu K/mol and $\theta = -3.6$ K. The effective magnetic moment is 1.75 BM.

The UV spectra of another new monoanion complex salt (n-Bu_4N)[Ni(dmbbip)$_2$] (**12**) show a broad band with medium intensity at 982 nm. It is further oxidized to yield a partially oxidized salt (n-Bu_4N)$_{0.59}$-[Ni(dmbbip)$_2$] (**13**) by treating with a stoichiometric amount of n-Bu_4NBr_3 The black powder of **13** is soluble in chloroform and its UV spectra have almost the same band profiles as those of the monovalent salt **12** where the low-lying broad band at 983.5 nm is enhanced.

Conclusions

A conductive nickel dithiolene, (n-Bu_4N)$_{0.29}$-[Ni(dmbit)$_2$] (**11**) was prepared and its conduction property studied. Four-probe d.c. conductivity of the conglomerate of crystals shows a metallic behavior from r.t. down to 220±20 K at which it has a maximum conductivity of 1.35±0.35 S/cm. Below 42 K it shows another metallic conduction down to 22 K where it reaches another maximum of 0.24±0.09 S/cm. The UV spectral study revealed that π-electron delocalization on the ligand is enhanced through sulfur enrichment but it also tends to separate into two interacting parts upon incorporation of a benzene ring. From a cyclic voltammetry study the on-site Coulomb integrals of these Ni dithiolenes were found to be in accordance with their conductivity. The effective magnetic moment of (n-Bu_4N)[Ni(dmbit)$_2$] (**10**) was derived from a magnetic susceptibility study to be 1.74 BM, which is very close to the spin-only value (1.73 BM).

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