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A neutral bis(diethylthiotetrathiafulvalenyldiselenolato)nickel complex: a superior organic conductor to the corresponding dithiolato derivative

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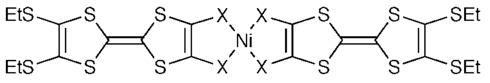
The tetra-*n*-hexylammonium salt of the bis(diethylthiotetrathiafulvalenyldiselenolato)nickelate complex monoanion (**1b**) was obtained by the reaction of bis(tetra-*n*-hexylammonium) diethylthiotetrathiafulvalenyldiselenolate with nickel(II) acetylacetonate. X-Ray structure analysis of **1b** showed that the molecular skeleton, except for the four ethyl groups, is almost planar, with the six sulfur and two selenium atoms on each ligand being essentially located in the same plane and with the geometry around the nickel atom being square-planar. From the SQUID and EPR measurements, the unpaired spin in **1b** is located primarily on the nickel atom, which is best described as a Ni(III) ($S = 1/2$) metal center. Iodine oxidation of **1b** gave the corresponding neutral complex **1a** as microcrystals. A compressed pellet of **1a** exhibited a room-temperature electrical conductivity of 2.8 S cm^{-1}, which is higher by *ca.* 60 times, than that for the corresponding dithiolato complex **2a** (5.0×10^{-2} S cm^{-1}) obtained by iodine oxidation of tetra-*n*-hexylammonium bis(diethylthiotetrathiafulvalenyldithiolato)nickelate **2b**. The temperature dependence of the electrical conductivity was as expected for a semiconductor, but the activation energy was very low (0.014 eV).

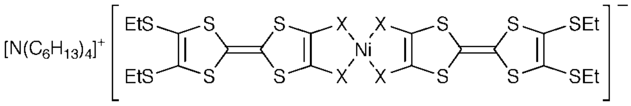
Introduction

The synthesis of new magnetic metal complexes involving both conducting π electrons and local d spins is of current interest, since novel electrical conducting and magnetic properties might be produced, if both types of electrons can significantly interact with each other.[1–8] As one of such π/d molecular systems, much attention has been directed toward neutral magnetic metal complexes with two tetrathiafulvalenyldithiolato groups.[9–13] The nickel complex first synthesized by Underhill and coworkers exhibited a considerably high electrical conductivity (*ca.* 0.1 S cm^{-1}) at room temperature, and the temperature dependence of the electrical conductivity was metal-like, albeit in a very narrow temperature range (275–300 K).[10] This finding was very noteworthy and suggested the possibility of single-component organic metals by investigating similar neutral complexes containing other magnetic metal atoms. With the aim to search for single-component organic metals to clarify the interaction between conducting π electrons and metal d spins in the neutral complexes, we had previously synthesized neutral bis(diethylthiotetrathiafulvalenyldithiolato)copper[12] and cobalt complexes,[13] and investigated their electrical-conducting and magnetic properties. Only a very small amount of spin resided on the copper atoms for the highly electrically conducting copper complex (3.7 S cm^{-1}), while for the insulating cobalt complex spin localization on cobalt was dominant. These results showed that preferential participation of either the conducting π electrons or local d spins is determined by the nature of the magnetic metal atom involved in complex formation.

The use of metal bound selenium atoms in place of sulfur atoms is expected to be a possible approach to lead to two comparable contributions of conducting π electrons and local d spins in π/d molecular systems, since the orbital overlap is less effective for the metal–selenium bond than for the metal–sulfur bond. Here, we report the synthesis of complexes **1a** and **1b**, and their electrical conduction and magnetic properties together with those of the corresponding dithiolato complexes **2a** and **2b**.



1a X = Se
2a X = S

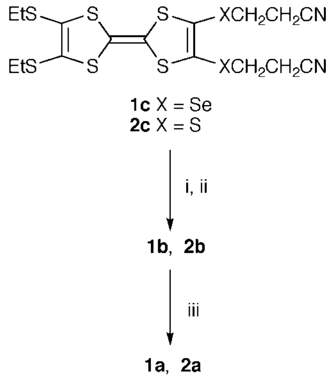


1b X = Se
2b X = S

Experimental

Synthesis of 1b and 2b

The synthetic procedure is shown in Scheme 1. A 25% (w/w) MeOH solution of tetramethylammonium hydroxide (0.2 ml, 0.4 mmol) was added to a mixture of bis(2′-cyanoethylseleno)-diethylthiotetrathiafulvalene[14] **1c** (111.7 mg, 0.2 mmol) and tetra-*n*-hexylammonium bromide (434.6 mg, 1.0 mmol) in MeOH (5 ml) under argon, and the reaction mixture was stirred at 0 °C for 2 h, followed by the addition of nickel(II) acetylacetonate (25.7 mg, 0.1 mmol) in MeOH (5 ml) and by further stirring overnight. The resultant precipitate was filtered off, washed with MeOH and finally dried *in vacuo* to give **1b** as a dark green solid in 89% yield. Recrystallization of the solid from CS_2 gave dark brown single crystals (mp > 300 °C). In a similar manner, **2b** was obtained as a brown solid in 37% yield by using bis(2′-cyanoethylthio)diethylthiotetrathiafulvalene[15]



Scheme 1 *Reagents and conditions*: i, tetramethylammonium hydroxide, tetra-*n*-hexylammonium bromide, MeOH, 0 °C, 2 h; ii, nickel(II) acetylacetonate, MeOH, 0 °C, overnight; iii, iodine, CS_2, room temperature.

2c (98.0 mg, 0.2 mmol), followed by recrystallization from CS_2 to give dark brown single crystals (mp >300 °C).

Synthesis of 1a and 2a

As also shown in Scheme 1, diffusion of iodine vapor to a CS_2 solution of **1b** (23.8 mg, 0.022 mmol) at room temperature gave black microcrystals of **1a** (mp >300 °C) in 67% yield. Anal. Calc. for $C_{20}H_{20}S_{12}Se_4Ni$: C, 23.56; H, 1.98. Found: C, 23.64; H, 1.88%. In a similar manner, **2a** was obtained by the iodine oxidation of **2b** (11.6 mg, 0.0098 mmol) as black microcrystals (mp >300 °C) in 72% yield. Anal. Calc. for $C_{20}H_{20}S_{16}Ni$: C, 28.87; H, 2.42. Found: C, 28.73; H, 2.56%.

X-Ray structure analysis

Intensity data were measured on a Rigaku AFC-7R automated four-circle diffractometer using graphite monochromated Cu-Kα radiation for **1b** and Mo-Kα radiation for **2b** at 20 °C. Empirical absorption corrections were performed in both cases. Experimental details and crystal data are given in Table 1. The structures were solved by direct methods (SIR92[16] and DIRDIF94[17]). Calculated positions of the hydrogen atoms [d(C–H) = 0.95 Å] were included in the final calculation. All the calculations were performed by using the teXsan crystallographic software package of the Molecular Structure Corporation.[18]

For **2b** the crystal data were of very low quality, so that the refinement was performed only with isotropic thermal parameters for all non-hydrogen atoms. For **1b** although the crystal was ideal being large and stable during measurement, there were 45% unobserved reflections using $1.0\sigma(F)$ as the observation criterion. In the high angle region ($\theta > 55°$) there were only 26% observed data, indicating a high degree of vibration. The structure shows remarkably high vibration of a tetra-*n*-hexylammonium ion (as also indicated by maxima from the difference map around carbon atoms near nitrogen atoms). Owing to this, some C–C bonds and conformations of the ion are unusual.

Table 1 Crystallographic data for **1b** and **2b**

	1b	**2b**
Formula	$C_{44}H_{72}S_{12}Se_4Ni$	$C_{44}H_{72}S_{16}Ni$
Formula weight, M	1374.32	1186.72
Crystal system	Monoclinic	Monoclinic
a/Å	35.437(5)	35.84(1)
b/Å	10.079(3)	9.96(1)
c/Å	17.512(3)	17.361(10)
β/°	106.65(1)	107.64(3)
V/Å^3	5992(2)	5908(7)
T/°C	20	20
Space group	$C2/c$	$C2/c$
Z	4	4
μ/cm^{-1}	73.75	9.24
Total reflections	5606	3045
Reflections used	3277	920
R_{int}	0.067	0.039
R, Rw	0.065, 0.098	0.133, 0.156

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/185. See http://www.rsc.org/suppdata/jm/1999/2979/ for crystallographic files in .cif format.

Electrical conductivity, magnetic susceptibility and EPR measurements

Electrical conductivities were measured on single crystals or compressed pellets by using a four-probe method in the temperature range 70–300 K. Electrode contacts were made by using gold paste. Magnetic susceptibilities (χ_{obs}) were measured in the temperature range 1.8–300 K under an applied field of 1 kOe using a SQUID magnetometer (MPMS XL, Quantum Design). The paramagnetic susceptibility (χ_p) was obtained by subtracting the diamagnetic contribution calculated from Pascal's constants[19] from χ_{obs}. The EPR spectrum was recorded by using a JEOL 1X spectrometer with Mn^{2+}/MgO as a calibrant.

Results and discussion

Molecular and crystal structures

Fig. 1 shows the molecular structures of **1b** and **2b**. Selected bond distances and angles for **1b** are listed in Table 2. The

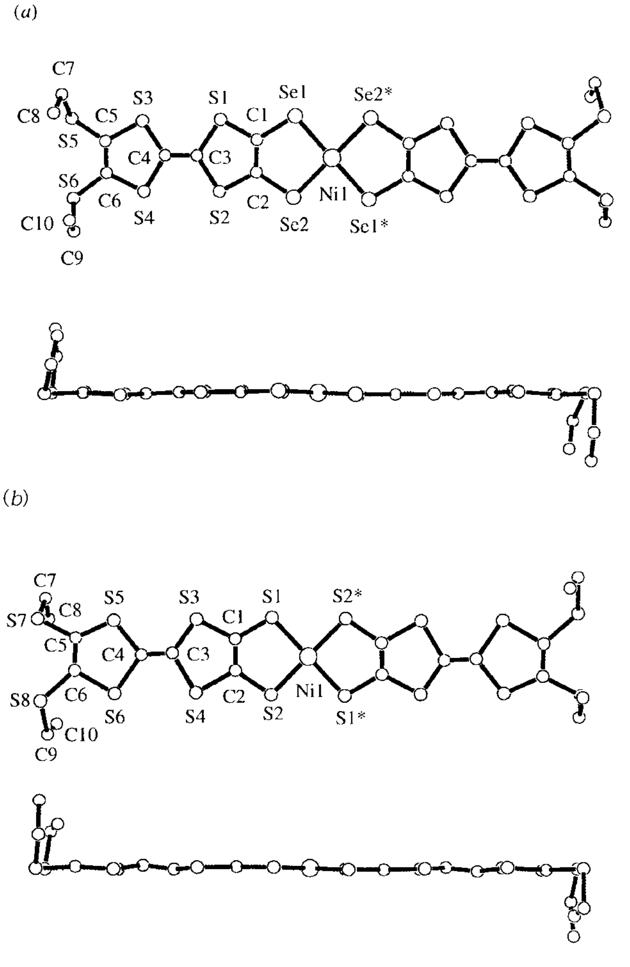


Fig. 1 Molecular structures of the anion moieties for (a) **1b** and (b) **2b**.

Table 2 Selected bond distances (Å) and angles (°) for **1b**

Ni(1)–Se(1)	2.2831(9)	S(4)–C(4)	1.756(9)
Ni(1)–Se(1)	2.269(1)	S(4)–C(6)	1.73(1)
Se(1)–C(1)	1.865(8)	S(5)–C(5)	1.75(1)
Se(2)–C(2)	1.868(8)	S(5)–C(7)	1.85(2)
S(1)–C(1)	1.733(8)	S(6)–C(6)	1.77(1)
S(1)–C(3)	1.751(9)	S(6)–C(9)	1.84(2)
S(2)–C(2)	1.738(8)	C(1)–C(2)	1.360(10)
S(2)–C(3)	1.769(8)	C(3)–C(4)	1.36(1)
S(3)–C(4)	1.713(9)	C(5)–C(6)	1.34(1)
S(3)–C(5)	1.74(1)		
Se(1)–Ni(1)–Se(2)	93.47(3)	Ni(1)–Se(2)–C(2)	101.4(2)
Se(1)–Ni(1)–Se(2*)	86.53(3)	Se(1)–C(1)–C(2)	120.8(6)
Ni(1)–Se(1)–C(1)	101.8(2)	Se(2)–C(2)–C(1)	122.4(5)

average Ni–Se bond length is 2.276(1) Å, which is very close to the corresponding values found for bis(diselenolato)nickel complexes such as tetra-*n*-butylammonium bis(1,3-dithiole-2-selone-4,5-diselenolato)nickelate [2.276(2) Å][20] and tetraethylammonium bis(5,6-dihydro-1,4-dithiin-2,3-diselenolato)nickelates [2.272(2) Å].[21] The bond angles around the Ni atom are 93.47(3)° [Se(1)–Ni(1)–Se(2)] and 86.53(3)° [Se(1)–Ni(1)–Se(2*)], indicating that the geometry around the Ni atom is virtually square–planar. Furthermore, each of the tetrathiafulvalene moieties involving two sulfur and two selenium atoms or four sulfur atoms have high planarity (mean deviation from the plane is 0.0313 Å for **1b**), so that the whole molecular skeleton, except for the four ethyl groups, is almost planar. Packing views projected on the *ac* and *bc* planes are shown in Fig. 2. Each nickelate ion in **1b** and **2b** is surrounded by four tetra-*n*-hexylammonium ions and there are no close contacts between the nickelate ions. The two different arrangements of nickelate ions are present in the crystal. One arrangement has a *ca.* 45° dihedral angle to the *ac* plane while the other has a *ca.* 45° dihedral angle to the *ab* plane. As a result, the two arrangements are almost perpendicular to each other.

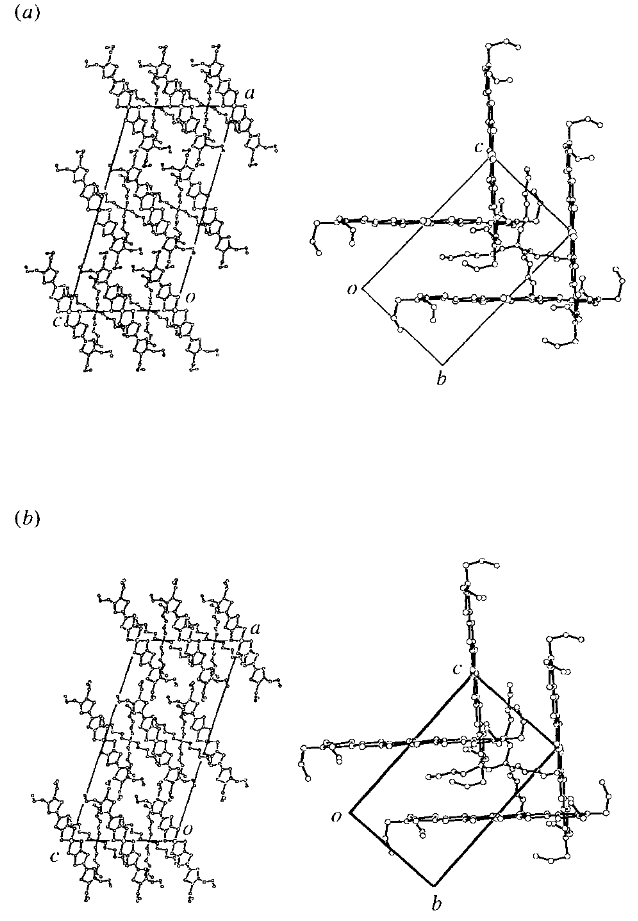


Fig. 2 Crystal structures of (a) **1b** and (b) **2b**.

An X-ray structure analysis of **1a** was unsuccessful despite many attempts to obtain a single crystal of suitable size for the analysis. However, since the molecular structures of the nickelate ions are very similar in **1b** and **2b**, it is anticipated that the molecular structure of **1a** should by very similar to that of **2a**, the X-ray structure analysis of which has previously been performed.[10] The molecular skeleton of **2a** is almost planar, except for the four ethyl groups, which are projected by an angle of *ca.* 102° out of molecular plane. Furthermore, in **2a**, molecules are stacked with an interplanar distance of *ca.* 3.4 Å in a slightly slipped manner, and close intercolumnar contacts are present between the dithiolato sulfur atoms and also between the tetrathiafulvalenyl sulfur atoms and the dithiolato sulfur atoms. For **1a** such intra- and inter-columnar contacts might be more effective than for **2a**, since the van der Waals' radius (2.00 Å) of selenium is larger than that (1.85 Å) of sulfur.

Electrical conductivity

Electrical conductivity measurements were performed on single crystals for **1b** and **2b**, and on compressed pellets for **1a** and **2a**. Table 3 reports room-temperature electrical conductivities (σ_{RT}), which are 2.8, $<10^{-10}$, 5.0×10^{-2} and $<10^{-10}$ S cm^{-1} for **1a**, **1b**, **2a** and **2b**, respectively. The value of σ_{RT} for **2a** obtained in this experiment was comparable to the value on the compressed pellet (1.0×10^{-1} S cm^{-1}) already reported.[10] It should be noted that σ_{RT} of **1a** is higher by *ca.* 60 times than that of **2a**. For **1a** the temperature dependence of σ was semiconducting, and the σ *vs.* T plot obeyed an equation of the form $\sigma = A\exp(E_a/kT)$, where A is a constant, E_a is the activation energy (0.014 eV) and k the Boltzmann constant. Electrical conducting properties as measured on a compressed pellet of **1a** are not intrinsic. However, the present results lead to an expectation that the selenium atoms bound to nickel might significantly increase the electrical conductivity relative to the corresponding sulfur atoms in the single crystals of **1a** and **2a**. Since the crystal structure of **1a** is, as yet, not known, no definitive comment can be made about the effect of the selenium atoms, although it is considered that the most important factor is the larger van der Waals' radius of selenium (2.00 Å)[22] relative to sulfur (1.85 Å).[22]

Magnetic susceptibilities

For **1b** and **2b** the temperature dependences of χ_{p} obeyed a Curie–Weiss law, $\chi_{\mathrm{p}} = C/(T-\theta)$, where C is the Curie constant and θ the Weiss temperature. The best-fitting result was for $C = 0.36$ emu K mol^{-1} and $\theta = -2.9$ K for **1b**, and $C = 0.34$ emu K mol^{-1} and $\theta = -2.6$ K for **2b**. The C and θ values obtained suggest that an almost complete $S = 1/2$ spin resides on each nickel complex and that the intermolecular spin–spin interaction is weakly antiferromagnetic. Such spin–spin interactions in **1b** and **2b** can be well understood from their

Table 3 Electrical conductivities for **1a**, **1b**, **2a** and **2b** at room temperature

Ni complex	σ_{RT}/S cm^{-1}	E_a/eV
1a	2.8^{a}	0.014
1b	$<10^{-10\,b}$	—
2a	$5.0\times10^{-2\,a}$	—
2b	$<10^{-10\,b}$	—

[a]Measured on a compressed pellet using the four-probe method. [b]Measured on a single crystal using the four-probe method.

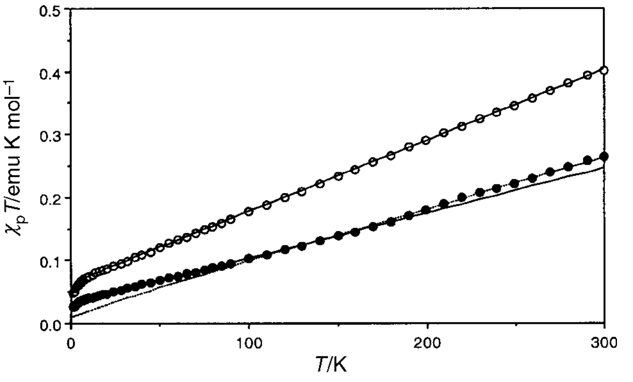


Fig. 3 Temperature dependences of $\chi_p T$ for (●) **1a** and (○) **2a**. The continuous and dashed lines were reproduced by choosing appropriate values of C, θ and χ_{const} in the equation $\chi_p(T) = C/(T-\theta) + \chi_{const}$.

crystal structures, in which there is no contact between the neighboring nickelate ions.

On the other hand, for **1a** and **2a** the $\chi_p T$ values gradually decreased with decreasing temperature from 300 to 1.8 K (Fig. 3). However, for **1a**, the $\chi_p T$ *vs.* T plot changed at 140 K. In the temperature regions 300–140 and 140–1.8 K, χ_p is composed of both a Curie–Weiss component and a temperature-independent susceptibility χ_{const}, *i.e.*, $\chi_p = C/(T-\theta) + \chi_{const}$. By choosing best-fitting C, θ and χ_{const} values in the above equation, the observed χ_p *vs.* T behavior was well reproduced in both temperature regions. The Curie constants obtained were 1.3×10^{-2} emu K mol^{-1} in the high temperature region and 3.1×10^{-2} emu K mol^{-1} in the low temperature region, which corresponds to 1.5 and 4.1%, respectively, of the total amount (0.413 + 0.375 = 0.788 emu K mol^{-1}) of non-interacting Ni(III) ($S = 1/2$) spins and π radical ($S = 1/2$) spins. A considerable part of the two spins present in each nickelate ion contributes to the electrical conduction in both temperature regions, and only a very small amount of spin remains within the Ni–Se vicinity. However, the marked difference in θ was evident: −40.4 K in the high temperature region and −0.68 K in the low temperature region. The χ_{const} values were similar: 8.1×10^{-4} emu mol^{-1} in the high temperature region and 7.2×10^{-4} emu mol^{-1} in the low temperature region. Judging from these results, the transition of magnetic properties at 140 K is obviously due to a change in antiferromagnetic interactions between the spins on the Ni atoms. Thus, a comparatively strong antiferromagnetic interaction ($\theta = -40.4$ K) is observed at $\geqslant$140 K while this interaction became very weak ($\theta = -0.68$ K) below 140 K. A possible explanation is that neighboring nickelate ions move away from each other at lower temperatures. For **2a** the χ_p *vs.* T behavior can also be well represented by equation $\chi_p = C/(T-\theta) + \chi_{const}$ in the whole temperature region with best-fitted C, θ and χ_{const} values of 6.4×10^{-2} emu K mol^{-1}, −0.21 K and 1.1×10^{-3} emu mol^{-1}, respectively; the value of C is equal to 8.1% of the total spin while the θ and χ_{const} values are similar to those of **1a**, suggesting that there is little difference in magnetic properties between **1a** and **2a**.

EPR spectra

The EPR microcrystal spectra of **1b** and **2b** measured at 297 K showed two signals: $g_\parallel = 2.105$ and $g_\perp = 2.060$ for **1b**, $g_\parallel = 2.069$ and $g_\perp = 2.024$ for **2b**. From comparison of the observed g values with those of the tetra-*n*-butylammonium bis(*cis*-stilbenedithiolato)nickelate complex,[23] **1b** and **2b** can be assigned as Ni(III) complexes. Since a large π-conjugated tetrathiafulvalenyl-diselenolato or -dithiolato ligand is bound to the nickel atom, the spin might be expected to be distributed to the tetrathiafulvalenyl moieties for **1b** and **2b**. However, the g values in **1b** and **2b** are very close to those of bis(ethylenedithiolato)- and bis(ethylenediselenolato)-nickel complexes, so that the spin appears to be entirely localized in the vicinity of the nickel atom.

On the other hand, the microcrystal EPR spectra of **1a** and **2a** were quite different from those of **1b** and **2b**. At 293 K one broad doublet signal was observed at $g = 2.0563$ ($\Delta H_{pp} = 568$ G) for **1a**, and at $g = 2.0141$ ($\Delta H_{pp} = 119$ G) for **2a**. Very similar spectra were also obtained at 77 K, although the broad signals were sharpened. As is obvious from the above SQUID results these signals are largely due to the conducting π electrons, and signals due to the very small amount of local spins are hidden within in the main signals because of their weak intensity. It should be noted that the g value of **1a** is larger than that of **2a**, suggesting that the selenium or sulfur atoms bound to the nickel atom also participate in the electron conduction, since a heavier selenium atom exerts a larger shift on g values than does sulfur.

Conclusion

In this study, the first neutral nickel complex with two diethylthiotetrathiafulvalenyldiselenolato groups, **1a**, was successfully prepared, although the corresponding dithiolato nickel (**2a**),[10] copper[12] and cobalt complexes[13] are already known. A compressed pellet of **1a** exhibited an σ_{RT} some 60 times higher than that of **2a**. In addition, the temperature dependence of σ was semiconducting, but the value of E_a was quite small. If single crystals can be prepared and electrical conductivity measurements performed, **1a** might prove to be metallike in behavior. The present study is significant in that it clearly demonstrates that selenium atoms bound to nickel exert an increased effect on the electrical conduction than do corresponding sulfur atoms. While the cause of this is not definitive, increased orbital overlap within and between columns is likely to be an influential factor.

Attempts to prepare neutral magnetic complexes with comparable contributions of conducting π electrons and local d spins were not successful. In both **1a** and **2a** a considerable part of the spin contributes to the electrical conduction, while only a very small amount (< 10%) of the spin resides on the nickel atoms. The degree of the orbital overlap in the Ni–Se bond is almost the same as found for the Ni–S bond. From the present and previous results, neutral complexes involving magnetic or non-magnetic metals with square-planar geometry can in general be regarded as π/d molecular systems, in which the sulfur or selenium π orbitals on the tetrathiafulvalenyl-dithiolato or -diselenolato group strongly interact with the d orbitals on the central metal atom.

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