# Synthesis, Structure, and Physical Properties of Tetraalkylammonium Bis(5,6-dihydro-1,4-dithiin-2,3-diselenolato)nickelate, $(R_4N)[Ni(ddds)_2]$ (R = Me, Et, and *n*Bu), and Neutral Complex $[Ni(ddds)_2]_2$

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Novel metal complexes $(R_4N)[Ni(ddds)_2]$ (R = Me, Et and *n*Bu, ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate) have been prepared and their crystal structures determined. The intraligand Se–Se distance is longer than that between the inner sulfur atoms of the five-member ring of the $M(dddt)_2^-$ sulfur analogue and is almost equal to the S–S distance in the six-member ring. Consequently, two-dimensional intermolecular close contacts are expected, and observed in $Ni(ddds)_2$ complexes. The neutral $Ni(ddds)_2$ species was obtained by electrochemical oxidation from the monoanionic $(nBu_4N)[Ni(ddds)_2]$ complex. X-Ray crystal structure analyses of this neutral species show that two $Ni(ddds)_2$ are connected by the two Ni–Se bonds. Thus, the $Ni(ddds)_2$ entities form $[Ni(ddds)_2]_2$ dimers which are arranged face-to-face and rotated by about 90° with respect to each other. The electrochemical behavior of $(nBu_4N)[Ni(ddds)_2]$ indicates the possible formation of cation-radical species. The room temperature magnetic susceptibility measurements showed that the $(R_4N)[Ni(ddds)_2]$ complexes are paramagnetic with $\mu_{eff}$ = 1.77–1.83 $\mu_B$, corresponding to one unpaired electron per molecular formula. The temperature dependence of the magnetic susceptibility of $(Et_4N)[Ni(ddds)_2]$ is indicative of weak long-range antiferromagnetic ordering below 9 K. The dimerization in $[Ni(ddds)_2]_2$ results in a strong antiferromagnetic spin coupling within the dimer, and explain the non magnetic state observed for this compound.

## Introduction

The development of new organic conductors has made great strides over the last two decades since the discovery in 1973 of the first synthetic metal, i.e., tetrathiafulvalene−tetracyano-*p*-quinodimethane(TTF·TCNQ).[1][2][3][4] Along this line, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) has taken a leading role, and a large number of new organic superconductors have been derived from this molecule.[5] On the other hand, the study of transition-metal bis(dithiolene) complexes has an even longer history[6][7] than that of the TTF-based systems and has been an area of great interest because the salts of these complexes show various crystal structures and conducting properties depending on the nature of the central metal atom and counter ion, and the oxidation state.[8] These salts show a tendency to form one-dimensional structure and, consequently, most of those that exhibit high metal-like conductivity at ambient pressure become insulator at low temperature. However, no less than eight superconductors have been discovered within the series of $M(dmit)_2$-based complexes (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate), namely, $(TTF)[Ni(dmit)_2]_2$, α- and α′-$(TTF)[Pd(dmit)_2]_2$, $(Me_4N)[Ni(dmit)_2]_2$, β-$(Me_4N)[Pd(dmit)_2]_2$, $(Et_2Me_2N)[Pd(dmit)_2]_2$, α-$(EDT\text{-}TTF)[Ni(dmit)_2]_2$,[9] and, most recently, β′-$(Et_2Me_2P)[Pd(dmit)_2]_2$.[10]

Among the many chemical modifications of $M(dmit)_2$ systems subsequently studied, metal complexes of 5,6-dihydro-1,4-dithiin-2,3-dithiolate $[M(dddt)_2]$ were synthesized for the first time about ten years ago.[11][12] They have a planar structure remarkably similar to that of BEDT-TTF in which the central C=C bond of BEDT-TTF is substituted by a metal ion. The neutral $M(dddt)_2$ complexes (M = Ni, Pd, Pt, and Au) may be used as donor components in the preparation of partially-oxidized conducting cation-radical salts (as for BEDT-TTF), some of them exhibiting metallic temperature dependence down to low temperature.[13] In this context, the development of selenium analogue compounds of $M(dddt)_2$ has attracted our interest because the expected increase of the dimensionality resulting from enhanced transverse chalcogen−chalcogen interaction obtained through selenium substitution. This increase of the dimensionality is known to stabilize the metallic state by suppressing low-dimensional instabilities (such as the Peierls transition[14]) at low temperature. For example, such a strong stabilization of metallic state has been observed in salts derived from BETS (BETS = bis(ethylenedithio)tetraselenafulvalene),[15] the selenium ana-

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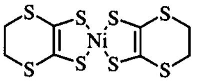
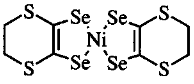
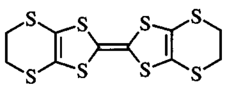
logue of BEDT-TTF, and new BETS-based organic superconductors have been recently discovered.[16] Thus, selenium substitution has been applied to Ni(dddt)$_2$ compounds and we report herein on the synthesis, structure and physical properties of new selenium containing metal complexes (R$_4$N)[Ni(ddds)$_2$] (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate; R = Me, Et, *n*Bu[17]) and of the neutral [Ni(ddds)$_2$]$_2$ complex.



Ni(dddt)$_2^-$



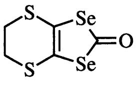
Ni(ddds)$_2^-$(**1**)



**BEDT-TTF**

## Results and Discussion

The synthesis of tetraalkylammonium salts of [Ni(ddds)$_2$]$^-$ **1** was performed as follows: the disodium diselenolate ligand, Na$_2$(ddds) **3**, was generated as a reddish orange solution by the hydrolytic cleavage of 4,5-ethylenedithio-1,3-diselenol-2-one **2** with 20% sodium ethoxide in dry THF at 0°C.[15b] Nickel complexes were obtained as the tetramethylammomium, tetraethylammonium and tetra-*n*-butylammonium salts, respectively, by successive treatment with an ethanol solution of nickel dichloride hexahydrate and the corresponding tetraalkylammonium bromide. The resulting precipitates were collected and washed with methanol and recrystallized in acetone or acetone/isopropanol (1:1) to afford dark green and air stable crystals. All the complexes were found by X-ray crystal analysis and elemental analysis to have a 1:1 cation/anion stoichiometry, indicating that the expected dianionic nickel complexes are easily air-oxidized to their monoanionic species in the course of preparation.



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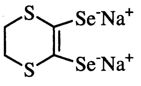


**3**

The neutral Ni(ddds)$_2$ species can be prepared by electrochemical oxidation of the monoanionic (*n*Bu$_4$N)[Ni(ddds)$_2$] complex in the presence of tetra-*n*-butylammonium perchlorate in acetonitrile. Needle-shaped black single crystals grew on the anode within about 2−3 weeks. In the course of research aiming at coupling [Ni(ddds)$_2$]$^-$ with nonlinear optical or magnetic cations,[18] the neutral Ni(ddds)$_2$ compound has been also unexpectedly obtained by electrochemical oxidation of (*n*Bu$_4$N)[Ni(ddds)$_2$] in the presence of (DAMP)I (4-dimethylamino-1-methylpyridinium iodide), (HPMS)(PF$_6$) {4′-[2(hydroxymethyl)pyrrolidinyl]-1-methylstilbazolium hexafluorophosphate} and [Cu(bpy)$_2$](PF$_6$)$_2$ (bpy = 2,2′-bipyridine). In the last case, two apparently different phases (needles and blocks) of the neutral complex were obtained. Finally, the Ni(ddds)$_2$ neutral complex can be also obtained as black powder by chemical oxidation by iodine of (*n*Bu$_4$N)[Ni(ddds)$_2$]. However, these powder material being extremely insoluble, the compound could not be recrystallized to obtain pure single crystal samples.

As previously reported,[17] the cyclic voltammogram of (*n*Bu$_4$N)[Ni(ddds)$_2$] shows two pairs of reversible redox waves corresponding to the [Ni(ddds)$_2$]$^{2-}$/[Ni(ddds)$_2$]$^-$ and [Ni(ddds)$_2$]$^-$/[Ni(ddds)$_2$] couples. The potentials of the first and second waves (−0.60 V and +0.16 V vs Ag/AgCl, respectively) are about 0.1 V higher than those of the (*n*Bu$_4$N)[Ni(dddt)$_2$] sulfur analogue (−0.71 and +0.03 V[11][12]), suggesting that selenium substitution results in a decrease of the electron-donating ability. The redox potential of the [Ni(ddds)$_2$]$^{2-}$/[Ni(ddds)$_2$]$^-$ couple (−0.60 V) is very low, especially when compared to that of the corresponding [Ni(dmit)$_2$]$^{2-}$/[Ni(dmit)$_2$]$^-$ couple (−0.18 V[9a]) and this accounts for the spontaneous air-oxidation of the expected dianionic (R$_4$N)$_2$[Ni(ddds)$_2$] salts observed during the synthesis. Moreover, the cyclic voltammogram of (*n*Bu$_4$N)[Ni(ddds)$_2$] also shows an irreversible oxidation wave at +0.71 V, reminiscent to that observed for (*n*Bu$_4$N)-[Ni(dddt)$_2$] (+0.99 V[11][12]), indicating the possible formation of cation-radical salts. Up to date, however, because of the low solubility of neutral Ni(ddds)$_2$, or the low stability of derived positively charged species, all attempts to grow crystals of such cation-radical salts failed.

Crystal structure analyses were performed for the monoanionic (R$_4$N)[Ni(ddds)$_2$] and neutral [Ni(ddds)$_2$] complexes. The crystal and experimental data are summarized in Table 4.

The molecular structure of the [Ni(ddds)$_2$]$^-$ anions and the atomic numbering schemes of the three studied (R$_4$N)[Ni(ddds)$_2$] complexes are shown in Figure 1. Selected bond lengths and angles are gathered in Tables 1 and 2. Very similar bond lengths are observed in the three cases. The average C=C double bond length in the [Ni(ddds)$_2$]$^-$ anions, 1.357 Å, is almost the same as in [Ni(dddt)$_2$]$^-$ anions, 1.363 Å,[11a][11d][11c] indicating a similar electronic state. The mean Ni−Se distance in the [Ni(ddds)$_2$]$^-$ anion, 2.27 Å, is longer than that of the corresponding Ni−S distance in the [Ni(dddt)$_2$]$^-$ anion, 2.132(9) Å,[11c] but the difference of both values (0.14 Å) is in fact almost equal to that between the atomic covalent radius of sulfur and selenium. The intramolecular Se−Se distances, Se(1)−Se(2) = 3.268(3) and Se(3)−Se(4) = 3.267(3) Å, are longer than that between the corresponding sulfur atoms of the inner five-member ring of [Ni(dddt)$_2$]$^-$, 3.068(3) Å,[11a] and are closer to the S−S distances in the outer six-member ring, S(1)−S(2) = 3.451(8) and S(3)−S(4) = 3.461(7) Å. This suggests that the expansion of the electron clouds of the chalcogen atoms is nearly uniform towards the transverse direction over the whole [Ni(ddds)$_2$]$^-$ anion, which is in contrast with the case of [Ni(dddt)$_2$]$^-$ (see below).

The overall structural arrangements of the three monoanionic (R$_4$N)[Ni(ddds)$_2$] complexes are also different

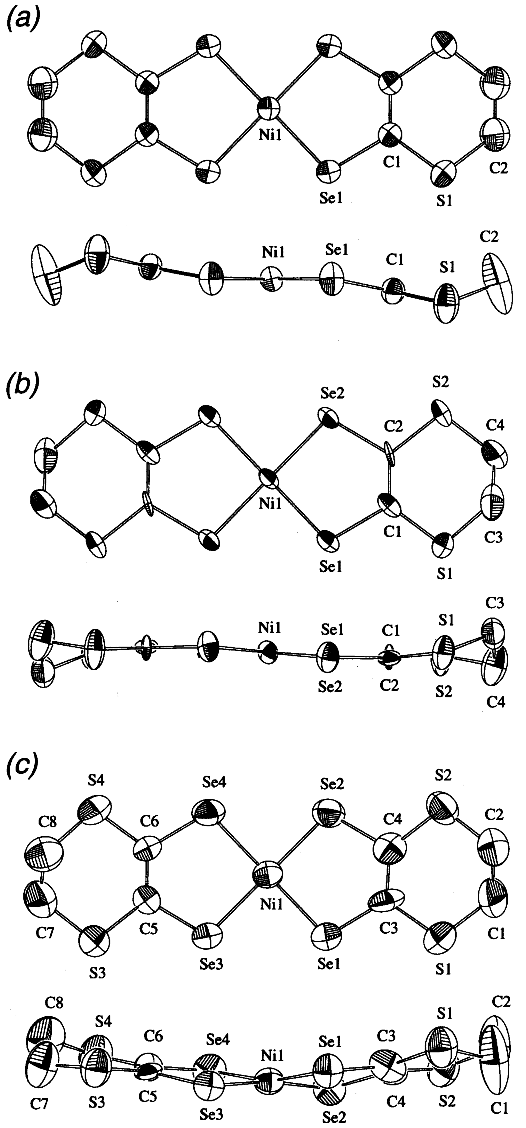


Figure 1. ORTEP drawings and atomic numbering schemes of the anion moieties (a) $(Me_4N)[Ni(ddds)_2]$, (b) $(Et_4N)[Ni(ddds)_2]$, and (c) $(nBu_4N)[Ni(ddds)_2]$

Table 1. Selected bond lengths [Å] for $Ni(ddds)_2$ complexes

| | $(Me_4N)$-$[Ni(ddds)_2]$ | $(Et_4N)$-$[Ni(ddds)_2]$ | $(nBu_4N)$-$[Ni(ddds)_2]$ | $[Ni(ddds)_2]_2$ |
|---|---|---|---|---|
| Ni(1)−Se(1) | 2.2672(8) | 2.284(3) | 2.263(3) | 2.332(1) |
| Ni(1)−Se(2) | | 2.259(2) | 2.270(3) | 2.311(1) |
| Ni(1)−Se(3) | | | 2.267(3) | 2.280(1) |
| Ni(1)−Se(4) | | | 2.268(3) | 2.284(1) |
| Se(1)−C(1) | 1.885(6) | 1.88(2) | | |
| Se(2)−C(2) | | 1.88(2) | | |
| Se(1)−C(3) | | | 1.84(2) | 1.881(8) |
| Se(2)−C(4) | | | 1.91(2) | 1.895(7) |
| Se(3)−C(5) | | | 1.89(2) | 1.871(7) |
| Se(4)−C(6) | | | 1.86(2) | 1.858(8) |
| C(1)−C(1)* | 1.35(1) | | | |
| C(1)−C(2) | | 1.35(2) | | |
| C(3)−C(4) | | | 1.37(2) | 1.368(10) |
| C(5)−C(6) | | | 1.36(2) | 1.384(10) |
| C(1)−S(1) | 1.746(6) | | | |
| C(3)−S(1) | | 1.80(2) | 1.79(2) | 1.718(8) |
| C(4)−S(2) | | 1.78(3) | 1.74(2) | 1.734(8) |
| C(5)−S(3) | | | 1.75(2) | 1.748(7) |
| C(6)−S(4) | | | 1.75(2) | 1.740(8) |
| S(1)−C(2) | 1.753(8) | | | |
| S(1)−C(1) | | 1.77(2) | 1.78(3) | 1.75(1) |
| S(2)−C(2) | | 1.75(2) | 1.76(2) | 1.77(1) |
| S(3)−C(7) | | | 1.80(2) | 1.79(1) |
| S(4)−C(8) | | | 1.81(2) | 1.76(1) |
| C(2)−C(2)* | 1.34(2) | | | |
| C(3)−C(4) | | 1.52(3) | | |
| C(1)−C(2) | | | 1.35(3) | 1.34(1) |
| C(7)−C(8) | | | 1.37(2) | 1.23(1) |

from those of the corresponding $R_4N[Ni(dddt)_2]$ (R = Me, Et, *n*Bu) sulfur analogues:[11a][11d][11c]

− $(Me_4N)[Ni(ddds)_2]$: One tetramethylammonium cation and one $[Ni(ddds)_2]^-$ anion are crystallographically independent. The Ni atom of $[Ni(ddds)_2]^-$ and the N(1) atom of the tetramethylammonium cation are located in the mirror plane (*ab* plane) and on the center of inversion. The C(4) atom of the tetramethylammonium cation is in the mirror *ab* plane. Therefore, the tetramethylammonium cation is octahedrally disordered. As shown in Figure 2a, the cations and anions are stacked alternately along the *b* axis and form a layered structure in the *ab* plane. Only the terminal ethylenedithio bridges are slightly overlapping each other. On the other hand, the $[Ni(ddds)_2]^-$ anions are arranged in a zigzag manner along the *c* axis and there is one short intermolecular Se(1)···S(1) contact [3.781(2) Å] between adjacent layers (Figure 2b). The $[Ni(ddds)_2]^-$ anion has a slightly chair-like structural arrangement with a dihedral angle of 11.01° and exhibits a completely planar coordination around the central nickel atom. The terminal C(2)−C(2)* bond length has a very short value, 1.34(2) Å, compared to the C−C single bond lengths (about 1.51 Å) usually observed in analog compounds.[11][12] The C(2) carbon atom has a large temperature factor [$B_{eq}$ = 10.7(4)], indicating a conformational flexibility of the ethylene bridge.

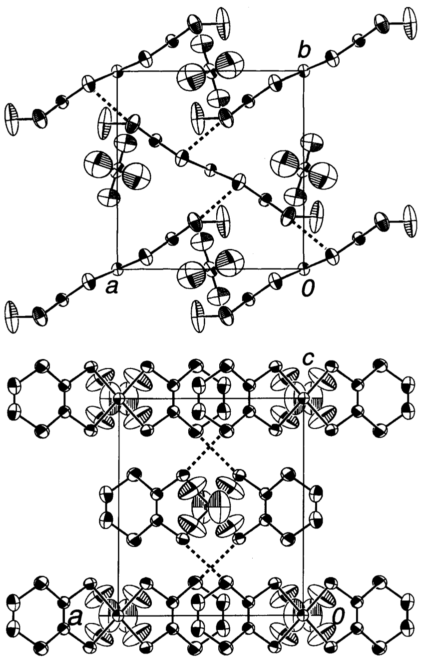
− $(Et_4N)[Ni(ddds)_2]$: The Ni atom of $[Ni(ddds)_2]^-$ is located on the center of inversion and the $[Ni(ddds)_2]^-$ anion moiety is almost planar except for the slightly staggered ethylene bridge. The N(1) atom of the tetraethylammonium cation is also located on the center of inversion and two carbon atoms connected to the nitrogen atom are disordered on two positions [C(5) and C(9), C(8) and C(10)] with occupancy factor of 0.5. The anions form a one-dimensional array along the *a*-axis and there are several intermolecular Se···Se or Se···S contacts between the adjacent anions, indicating strong side-by-side interaction along the *a* axis (Figure 3a). On the other hand, each donor array is completely separated by a layer containing the tetraethylammonium cations and there is no interaction between the anion layers (Figure 3b).

− $(nBu_4N)[Ni(ddds)_2]$: The unit cell contains one crystallographically independent tetrabutylammonium cation and one $[Ni(ddds)_2]^-$ anion. Figure 4 shows the projection onto the *bc* plane. Neither a stacking, nor a columnar structural arrangement of the anions is observed. Only one S···S contact [3.542(10) Å] between anions is found (dotted lines in Figure 4). Each anion is surrounded by a counter tetrabu-

Table 2. Bond angles [°] involving the nickel atom in Ni(ddds)$_2$ complexes

| | $(Me_4N)[Ni(ddds)_2]$ | $(Et_4N)[Ni(ddds)_2]$ | $(nBu_4N)[Ni(ddds)_2]$ | $[Ni(ddds)_2]_2$ |
|---|---|---|---|---|
| Se(1)−Ni(1)−Se(1) | 92.23(4) | | | |
| Se(1)−Ni(1)−Se(2) | | 88.28(8) | 92.2(1) | 90.80(5) |
| Se(2)−Ni(1)−Se(4) | | | 89.2(1) | 85.29(5) |
| Se(3)−Ni(1)−Se(4) | | | 92.2(1) | 91.39(5) |
| Se(1)−Ni(1)−Se(3) | | | 88.3(1) | 90.13(5) |
| Se(1)−Ni(1)−Se(2)* | | | | 90.43(5) |
| Se(2)−Ni(1)−Se(2)* | | | | 97.33(4) |
| Se(3)−Ni(1)−Se(2)* | | | | 89.83(4) |
| Se(4)−Ni(1)−Se(2)* | | | | 109.69(5) |
| Ni(1)−Se(1)−C(1) | 102.7(2) | 103.3(7) | | |
| Ni(1)−Se(2)−C(2) | | 103.7(5) | | |
| Ni(1)−Se(1)−C(3) | | | 102.6(5) | 102.0(2) |
| Ni(1)−Se(2)−C(4) | | | 103.2(6) | 102.7(2) |
| Ni(1)−Se(3)−C(5) | | | 102.6(5) | 103.4(2) |
| Ni(1)−Se(4)−C(6) | | | 103.6(5) | 103.1(2) |

Figure 2. Crystal structures of $(Me_4N)[Ni(ddds)_2]$ projected onto the (a) *ab*-plane and (b) *ac*-plane. − The intermolecular contact Se(1)−S(1) (−1/2 + *x*, 3/2 − *y*, 1/2 − *z*) is 3.781(2) Å



tylammonium cations. The nickel atom is coordinated to the four selenium atoms in a slightly distorted square planar geometry with a dihedral angle of 15.7° between the two five-member rings. This situation is different from that observed in the case of the other complexes with R = Me, Et, in which the coordination geometry around the nickel atom is strictly planar for symmetry reason. This is probably due to the steric hindrance of the bulky tetrabutylammonium cation. Each of the two chelating ligands is almost planar except for the ethylene bridge.

A stated above (see also Experimental Section), two, apparently different phases of the neutral Ni(ddds)$_2$ complex have been obtained, a needle-shaped one and a block-shaped one. The structures of these two phases have been independently determined and are in fact identical.[19] Two Ni(ddds)$_2$ units related by a center of inversion (symmetry

Figure 3. Crystal structures of $(Et_4N)[Ni(ddds)_2]$ projected onto the (a) *ab*-plane and (b) *bc*-plane. − The intermolecular contacts are Se(1)−S(2) (1 + *x*, *y*, *z*) = 3.750(7), Se(2)−S(2) (−*x*, 1 − *y*, −*z*) = 3.766(8), and Se(2)−Se(2) (−*x*, 1 − *y*, −*z*) = 3.975(5) Å. Two disordered carbons of cation moiety are omitted for clarity

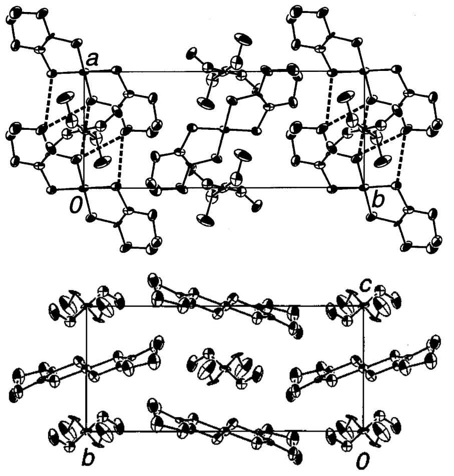
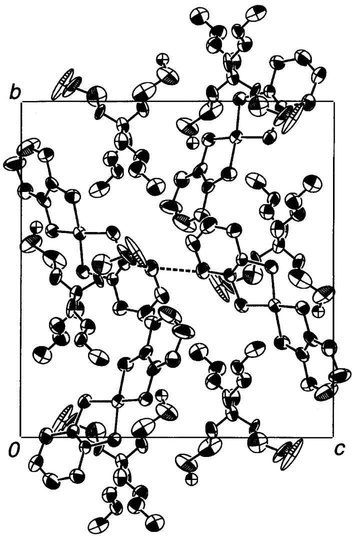


Figure 4. Crystal structure of $(nBu_4N)[Ni(ddds)_2]$ projected onto the *bc*-plane. − The intermolecular contact S(4)−S(4) (1 − *x*, −*y*, −*z*) is 3.542(10) Å



operation $1 - x$, $1 - y$, $2 - z$) are strongly dimerized and connected by the two Ni−Se(2) [2.496(1) Å] bonds to each other [the Ni(1)−Ni(1) distance is 3.178(2) Å]. Consequently, the neutral $Ni(ddds)_2$ complex should be more appropriately described as a dimer, $[Ni(ddds)_2]_2$ (Figure 5). The square coordination around nickel is distorted with a dihedral angle of 21.3°. Within each $Ni(ddds)_2$ entity of the dimer, the nickel atom is displaced by about 0.27 Å from the optimal plane of the four selenium atoms towards the axial selenium atom of the other $Ni(ddds)_2$ entity of the dimer. The large thermal ellipsoids of C(1), C(7) and C(8) and the small C(1)−C(2) and C(7)−C(8) distance indicate a conformational disorder of ethylene bridges. This disorder has been treated in the case of the block phase,[19] but no essential change in the description of the structure results from this treatment. The two ligand parts are heavily crooked and adopt a butterfly-wing shape conformation, probably caused by the steric hindrance introduced by the very short interplanar distance (2.84 Å for the $NiSe_4$ core of $Ni(ddds)_2$ entity). This structure is quite different from that reported for the neutral $Ni(dddt)_2$ analogue complex in which the $Ni(dddt)_2$ entities form uniform stacks and do not connect to each other[12], and rather resembles the dianion structure of $(Bu_4N)_2[Co(dddt)_2]_2$.[20] In $[Ni(ddds)_2]_2$, the $Ni(ddds)_2$ entities form real face-to-face dimers rotated by about 90° with respect to each other (Figure 6). This crystal structure is reminiscent of those reported for neutral BEDT-TTF,[21] or BETS,[15c], though in these compounds there are no actual chemical bonds between the two entities forming the so called "dimer". The $[Ni(ddds)_2]_2$ complexes are arranged side-by-side along the *a*-axis and produce a one-dimensional array. There are several Se(S)···Se(S) contacts between adjacent dimers as indicated by the dotted lines in Figure 7a. This is consistent with the value of the shape ratio $C$ {0.98 for the $Ni(ddds)_2$ entity in $[Ni(ddds)_2]_2$} which had been proposed to evaluate the possible extent of the transversal intermolecular interaction in such chalcogen-based compounds.[15c] This $C = 0.98$ value is very close to that calculated for a rectangular shape ($C = 1$), which is predicted as the most favorable one for high intermolecular interaction.

The bond lengths of the ddds ligands in $[Ni(ddds)_2]_2$ are nearly identical, within standard deviations, to those observed for the monoanionic $(R_4N)[Ni(ddds)_2]$ complexes. Especially the C=C double bond length does not change upon oxidation to the neutral species. These results indicate that the decrease of electron density does not occur within the ddds ligands, but it is the central nickel atom which is oxidized. This oxidation of nickel may explain the formation of a pentahedral intradimer coordination bond and the $[Ni(ddds)_2]_2$ dimer structure. Such a situation is quite different from that observed for the $Ni(dddt)_2$ sulfur analogue system. It was inferred from Raman spectra of $Ni(dddt)_2$ that nickel could be unambiguously described as a $d^8$ ion and that the dddt ligands were involved in oxidation and reduction.[22] Thus, substitution of selenium for sulfur atoms in the dddt ligand seems to affect coordination of the ligand to nickel and change the electron configuration of the resulting neutral complex.

Figure 5. (a) ORTEP drawing and atomic numbering scheme of the neutral $[Ni(ddds)_2]_2$ complex and (b) the side view. The second molecule is generated by symmetry operation $1 - x$, $1 - y$, $2 - z$

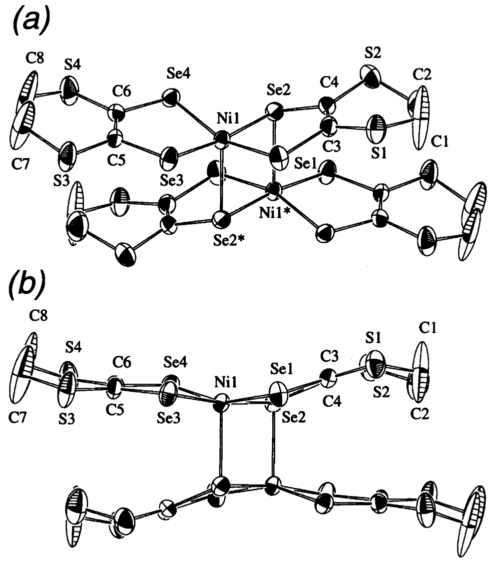
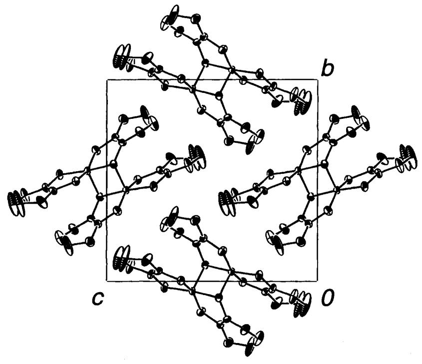


Figure 6. Crystal structure of neutral $[Ni(ddds)_2]_2$ projected onto the *bc*-plane



The room temperature magnetic susceptibilities of monoanionic $(R_4N)[Ni(ddds)_2]$ and neutral $[Ni(ddds)_2]_2$ complexes were measured by SQUID magnetometer at 1 Tesla. As shown in Table 3, all the monoanionic complexes show paramagnetism with $\mu_{eff} = 1.77 - 1.83\ \mu_B$ corresponding to one unpaired electron per molecular formula {1.73 $\mu_B$ for $s = 1/2$, $g = 2$ spins from the equation of $\mu_{eff}/\mu_B = g[s(s + 1)]^{1/2}$}. On the other hand, no magnetic moment was detected for the neutral $[Ni(ddds)_2]_2$ complex. This non-magnetic state can be explained by the stabilization of a singlet ground state in the $Ni(ddds)_2$ moiety, but more probably, as the X-ray results show that the $Ni(ddds)_2$ entities are structurally strongly dimerized in the neutral species, by a strong antiferromagnetic spin coupling within the dimer.

The temperature dependence of static magnetic susceptibility was measured for the monoanionic complexes. The tetramethylammonium salt showed a Curie-Weiss temperature dependence with a small positive Weiss temperature

Figure 7. Dimer array of neutral $[Ni(ddds)_2]_2$ (a) viewed along the molecular long axis and (b) projected onto the molecular plane. − The interdimer contacts are Se(1)−Se(4) (1 + *x*, *y*, *z*) = 3.993(1), Se(3)−S(4) (1 + *x*, *y*, *z*) = 3.663(3), Se(3)−Se(4) (1 + *x*, *y*, *z*) = 3.807(2), S(3)−S(4) (1 + *x*, *y*, *z*) = 3.639(4), and Se(2)−Se(4) (−*x*, 1 − *y*, 2 − *z*) = 3.897(2) A

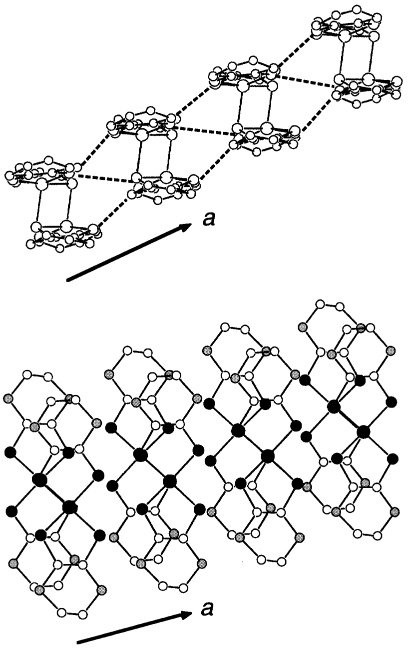


Table 3. Magnetic Properties of $(R_4N)[Ni(ddds)_2]$ at 1 Tesla.

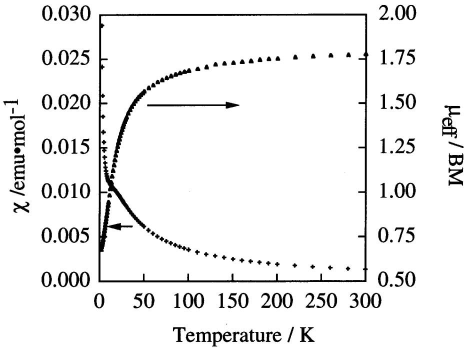
| | Magnetic susceptibility/ $\mu_B$ at room temperature | Weiss temperature/ K[a] |
|---|---|---|
| $(Me_4N)[Ni(ddds)_2]$ | 1.81 | +1.0 |
| $(Et_4N)[Ni(ddds)_2]$ | 1.77 | −18.0 |
| $(nBu_4N)[Ni(ddds)_2]$ | 1.83 | −4.0 |

[a] Weiss temperature was obtained from the Curie-Weiss law.

(θ = +1.0 K), indicating a slight short-range ferromagnetic interaction between anions. The tetrabutylammonium salt also obeyed a Curie-Weiss law, but the Weiss temperature is −4.0 K indicative of a weak antiferromagnetic interaction. However, both these salts did not show any phase transitions down to 2 K.

By contrast, the magnetic moment of the tetraethylammonium complex decreases as temperature decreases and a strong antiferromagnetic interaction is observed, as indicated by a large Weiss temperature of θ = −18 K in the high temperature region (Figure 8). Furthermore, the temperature dependence suddenly changes around 10 K, and below 9 K the magnetic susceptibility indicates a slight field dependence under magnetic fields below 100 Gauss, suggesting the occurrence of a weak long-range antiferromagnetic ordering. This phenomenon seems to be derived from the side-by-side strong interaction along the one-dimensional array of anions of $(Et_4N)[Ni(ddds)_2]$ (vide supra). A similar situation has been reported for the tetraethylammonium salt of $Ni(dddt)_2$.[11a]

Figure 8. Temperature dependence of magnetic susceptibility and magnetic moment of $(Et_4N)[Ni(ddds)_2]$ measured at 1 Tesla



## Conclusions

The selenium substitution of inner sulfur atoms in $Ni(dddt)_2$ complexes was expected to increase the transverse intermolecular interaction and therefore to stabilize metallic state. Indeed, in the resulting $Ni(ddds)_2$ complexes studied in this work, the intraligand Se−Se distance is longer than that of the corresponding inner sulfur atoms in the $M(dddt)_2$ complexes and is almost equal to the S−S distance in the outer six-member ring. Thus, two-dimensional intermolecular close contacts were expected and observed in the $Ni(ddds)_2$ complexes. This intermolecular interaction accounts for the strong antiferromagnetic interaction and weak long-range antiferromagnetic ordering observed for $(Et_4N)[Ni(ddds)_2]$. The neutral $Ni(ddds)_2$ species was obtained by electrochemical oxidation from the monoanionic $(nBu_4N)[Ni(ddds)_2]$ complex. X-Ray crystal structure analyses revealed that in this neutral species intermolecular Ni−Se bonds are formed, resulting in a $[Ni(ddds)_2]_2$ dimer compound. Given the promising CV data indicating the possible formation of cation−radical salts, several attempts, using various electrochemical procedures, were made to prepare such cation−radical salts starting from the neutral $[Ni(ddds)_2]_2$ molecule, but they all failed. This is probably due to the low solubility of $[Ni(ddds)_2]_2$ in common solvents. However, changing the nature of the metal may alleviate this difficulty and we are now engaged in the preparation of other $M(ddds)_2$ complexes such as those with M = Au.

## Experimental Section

*General*: Microanalyses were performed by the Organic Elemental Analysis Center, Department of Chemistry, School of Science, the University of Tokyo, and by the Microanalyses Service at the LCC-CNRS, Toulouse. − $^1H$ NMR: JEOL FT-NMR EX-270N (270 MHz for $^1H$ ), $[D_6]$acetone as solvent, TMS as internal standard. − IR: PERKIN-ELMER FTIR-1600.

4,5-Ethylenedithio-1,3-diselenol-2-one was synthesized by literature methods.[15b] THF was distilled over sodium and benzophenone and acetonitrile was distilled over calcium hydride under

Table 4. Crystallographic data for Ni(ddds)$_2$ complexes

| | $(Me_4N)[Ni(ddds)_2]$ | $(Et_4N)[Ni(ddds)_2]$ | $(Bu_4N)[Ni(ddds)_2]$ | $[Ni(ddds)_2]_2$ [19] |
|---|---|---|---|---|
| formula | $C_3H_5N_{0.25}Ni_{0.25}SSe$ | $C_8H_{14}N_{0.5}Ni_{0.5}S_2Se_2$ | $C_{24}H_{44}NNiS_4Se_4$ | $C_8H_8NiS_4Se_4$ |
| crystal color, habit | black, needle | black, plate | black, plate | black, needle |
| crystal system | orthorhombic | monoclinic | monoclinic | monoclinic |
| formula weight | 170.27 | 368.59 | 849.40 | 606.93 |
| $a$/Å | 9.464(3) | 8.022(1) | 9.668(5) | 6.589(3) |
| $b$/Å | 10.052(4) | 18.350(2) | 19.260(3) | 14.722(2) |
| $c$/Å | 11.166(2) | 8.733(2) | 18.099(2) | 15.366(1) |
| $\beta$/° | | 107.90(2) | 97.87(2) | 90.86(2) |
| $V$/Å$^3$ | 1062.2(9) | 1223.3(4) | 3338(1) | 1490.5(6) |
| space group | $P$nnm | $P2_1$/n | $P2_1$/c | $P2_1$/n |
| $Z$, formula units | 8 | 4 | 4 | 4 |
| $D_{calc}$/g·cm$^{-3}$ | 2.129 | 2.001 | 1.690 | 2.705 |
| dimensions, mm | 0.40 × 0.10 × 0.10 | 0.40 × 0.15 × 0.03 | 0.60 × 0.20 × 0.05 | 0.40 × 0.10 × 0.10 |
| $\mu$/cm$^{-1}$ | 81.56 | 70.90 | 52.08 | 116.05 |
| $2\theta_{max}$/° | 59.9 | 50.0 | 55.0 | 60.0 |
| total reflections | 1797 | 2235 | 7698 | 4520 |
| reflections used | 635 ($I$>3.0$\sigma$($I$)) | 815 ($I$>3.0$\sigma$($I$)) | 2359 ($I$>3.0$\sigma$($I$)) | 2318 ($I$>3.0$\sigma$($I$)) |
| parameters/$Fo$ | 10.58 | 5.86 | 7.66 | 15.05 |
| scan width | 1.15+0.50 tan$\theta$ | 1.26+0.50 tan$\theta$ | 0.94+0.50 tan$\theta$ | 1.37+0.50 tan$\theta$ |
| $\omega$ scan speed | 8.0° min$^{-1}$ | 8.0° min$^{-1}$ | 8.0° min$^{-1}$ | 8.0° min$^{-1}$ |
| $R$ [a], $R_w$ [b] | 0.039, 0.029 | 0.059, 0.057 | 0.065, 0.054 | 0.040, 0.033 |
| GOF | 1.57 | 1.63 | 2.65 | 1.54 |
| Max/min transmission | 1.00/0.90 | 1.00/0.52 | 1.00/0.47 | 1.00/0.79 |
| $T$/K | 296 | 296 | 296 | 296 |

[a] $R=\Sigma||Fo| - |Fc||/\Sigma|Fo|$. − [b] $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2}$.

nitrogen and stored in the refrigerator until use. Tetra-*n*-butylammonium perchlorate was recrystallized from ethyl acetate, and dried in vacuo. All other reagents were used without purification.

*Synthesis of* $(Me_4N)[Ni(ddds)_2]$: 4,5-Ethylenedithio-1,3-diselenol-2-one (0.302 g; 1.00 mmol) was hydrolyzed with a 20% ethanol solution of sodium ethoxide (1.50 g; 4.40 mmol) in dry THF (10.0 ml), at 0°C and under nitrogen. The color of the solution changed from yellow to reddish-orange as the reaction proceeded. The solution was stirred for 2 hours and a reddish-pink precipitate formed. A solution of nickel(II) chloride hexahydrate (0.128 g; 0.538 mmol) in ethanol (30.0 ml) was added dropwise to the reaction mixture and the resulting solution was stirred for 2 hours at 0°C. The obtained dark brown solution was treated with a solution of tetramethylammonium bromide (0.172 g; 1.12 mmol) in ethanol (10.0 ml), for 1 hour at 0°C, and warmed to room temperature. The resulting dark green precipitate was collected by filtering, washed with methanol and recrystallized from acetone to afford 0.240 g (0.352 mmol) of air-stable needle-shaped dark green crystals in 71% yield. − $C_{12}H_{20}NNiS_4Se_4$ (681.08): calcd. C 21.16, H 2.96, N 2.06, S 18.83, Se 46.37; found C 21.30, H 2.85, N 2.17, S 18.56, Se 46.79. − $\tilde{\nu}$ (KBr) = 2904 cm$^{-1}$, 1472, 1397, 1278, 1164, 943, 678.

The other $(R_4N)[Ni(ddds)_2]$ complexes with R = Et and *n*Bu were obtained by a procedure similar to that described above for $(Me_4N)[Ni(ddds)_2]$:

*Synthesis of* $(Et_4N)[Ni(ddds)_2]$: Obtained from 4,5-ethylenedithio-1,3-diselenol-2-one (0.303 g; 1.00 mmol), a 20% ethanol solution of sodium ethoxide (1.47 g; 4.31 mmol), a solution of nickel (II) chloride hexahydrate (0.126 g; 0.531 mmol) in ethanol (20.0 ml) and a solution of tetraethylammonium bromide (0.219 g; 1.04 mmol) in ethanol (20.0 ml), as air-stable plate-shaped dark green crystals in 82% yield (0.301 g, 0.408 mmol) − $C_{16}H_{28}NNiS_4Se_4$ (737.18): calcd. C 26.07, H 3.83, N 1.90, S 17.40; found C 26.12, H 3.74, N 2.18, S 17.35. − $\tilde{\nu}$ (KBr) = 2968 cm$^{-1}$, 2912, 1474, 1398, 1280, 1172, 999, 870, 780.

*Synthesis of* $(nBu_4N)[Ni(ddds)_2]$: Obtained from 4,5-ethylenedithio-1,3-diselenol-2-one (0.308 g; 1.02 mmol), a 20% ethanol solution of sodium ethoxide (1.41 g; 4.13 mmol), a solution of nickel (II) chloride hexahydrate (0.120 g; 0.505 mmol) in ethanol (30.0 ml) and a solution of tetrabutylammonium bromide (0.172 g; 0.534 mmol) in ethanol (10.0 ml), as air-stable plate-shaped dark green crystals in 84% yield (0.362 g, 0.426 mmol). − $C_{24}H_{44}NNiS_4Se_4$ (849.40): calcd. C 33.94, H 5.22, N 1.65, S 15.10; found C 33.67, H 5.20, N 1.61, S 15.08. − $\tilde{\nu}$ (KBr) = 2954 cm$^{-1}$, 2923, 2866, 1408, 1377, 1282, 687, 682. − $^1$H NMR $\delta$ = 3.39 (m, 8 H, $SCH_2CH_2S$), 1.87 (m, 8 H, $NCH_2$), 1.82 (m, 8 H, $NCH_2CH_2$), 1.50 (m, 8 H, $NCH_2CH_2CH_2$), 1.03 (m, 12 H, $CH_3$).

*Electrochemical Synthesis of* $[Ni(ddds)_2]_2$

*Method A:* $(nBu_4N)[Ni(ddds)_2]$ (10 mg) and tetra-*n*-butylammonium perchlorate (51 mg) were dissolved in 15 ml of acetonitrile under nitrogen. Electrochemical oxidation of this solution was carried out with a constant current of 1.0 μA at room temperature. Needle-shaped black single crystals grew on the anode within about 2−3 weeks.

*Method B:* A solution of $(nBu_4N)[Ni(ddds)_2]$ (15 mg) in acetonitrile (11 ml) was prepared under nitrogen and placed in the anodic compartment of a U-shaped electrochemical cell. A solution of $Cu(bpy)_2(PF_6)_2$ (14 mg) in acetonitrile was prepared under nitrogen and placed in the cathodic compartment of the cell. Electrochemical oxidation was carried out with a constant current of 0.25 μA at room temperature. Needle-shaped black and block-shaped black single crystals grew on the anode and on the low porosity glass frit between the anodic and cathodic compartments within about ten days.

In both cases, the obtained crystals were filtered, washed with ethanol, and air-dried at room temperature. − $C_{16}H_{16}Ni_2S_8Se_8$ (1213.86): calcd. C 15.83, H 1.35; found C 16.30, H 1.35. − $\tilde{\nu}$ (KBr) = 2945 cm$^{-1}$, 2906, 2866, 1365, 1324, 1272, 679, 668.

*Electrochemical Measurements:* Cyclic voltammetry data were obtained using a BAS 100B/W electrochemical workstation. The measurements were performed at 20°C in benzonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte with platinum working- and counter-electrode, and a BAS RE-1B Ag/AgCl reference electrode (scan rate: 200 mV $s^{-1}$).

*Magnetic Susceptibility Measurements:* Magnetic susceptibility measurements of $(R_4N)[Ni(ddds)_2]$ (R = Me, Et, *n*Bu) and $[Ni(ddds)_2]_2$ were performed on Quantum Design MPMS2 and MPMS7 magnetometers in the temperature range from 2 K to 300 K. The samples were wrapped with a clean aluminum foil whose magnetic susceptibility was separately measured and subtracted. The diamagnetic contribution was calculated from the Pascal's constants.

*X-Ray Crystallographic Studies:* Data collection for the $(R_4N)[Ni(ddds)_2]$ and needle-shaped crystals of $[Ni(ddds)_2]_2$ was performed on a Rigaku AFC-5R diffractometer with graphite monochromated Mo-*Kα* radiation (λ = 0.71069 Å) and a rotating anode generator. Intensities were collected by the ω-2θ scan technique. Lorentz-polarization (Lp) correction and empirical absorption correction based on azimuthal scans of several reflections were applied. The experimental details and crystal data are listed in Table 4. The structure was solved by direct method (MULTAN88[23] for neutral $[Ni(ddds)_2]_2$ and SHELXS86[24] for other complexes). The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[25] The non-hydrogen atoms were anisotropically refined by full-matrix least-squares method. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Cooperation[26]. Data collection for the block-shaped crystals of $[Ni(ddds)_2]_2$ was performed on a STOE IPDS (imaging plate diffraction system) using monochromatic Mo-*Kα* radiation (λ = 0.71013 Å), The structure was solved by direct methods (SHELXS-86[24]). Crystal data are given in ref.[19]. Experimental details, atomic coordinates, bond lengths and angles can be found in the Supporting Information section. Crystallographic data (excluding structure factors) for the structures reported in this manuscript have been deposited with the Cambridge Crystallographic Data Centre. The deposition numbers are CCDC-101694, -101695, and -101696 for the $(R_4N)[Ni(ddds)_2]$ (R = Me, Et, *n*Bu) compounds, respectively, 101697 for the needle-shaped $[Ni(ddds)_2]_2$, and 101556 for the block-shaped $[Ni(ddds)_2]_2$. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB12 1EZ [Fax: (internat.) + 44(0)1223/336−033, E-mail: deposit@ccdc.cam.ac.uk].

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[19] *Crystal Data*: black block, $C_8H_8Se_4S_4Ni$, $M = 607.0$, monoclinic, space group $P2_1/n$, unit cell at 160K: $a = 6.539(1)$, $b = 14.639(2)$, $c = 15.324(2)$ Å, $\beta = 90.62(2)°$, $V = 1466.8$ Å$^3$, $D_c = 2.75$ g/cm$^3$ for $Z = 4$. $\mu_c = 116.8$ cm$^{-1}$ corrections from absorption effects. 2218 independent reflections with $I > 0\ \sigma(I)$. The non-hydrogen atoms were refined anisotropically. Disorder has been treated on two carbons C(7), C(8) of one terminal ethylene group. Hydrogens atoms were included but not refined. The

structure was refined by full-matrix least squares to $R = 0.035$, $R_w = 0.029$. Atomic coordinates, bond lengths and angles, and thermal parameters are available in the Supporting Information.

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