Synthesis, structure and physical properties of the new selenium containing metal complex $NBu_4[Ni(ddds)_2]$ (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate)

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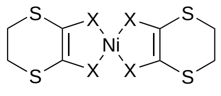
The synthesis, structure and physical properties of the new selenium containing metal complex $NBu_4[Ni(ddds)_2]$ (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate) are described.

In the past two decades development of new organic conductors has undergone rapid progress. Among them, conductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) have played a key and major role in the search for new organic superconductors.[1] On the other hand bis(dithiolene) metal complexes are also of great interest because they show a variety of crystal structures and conducting properties upon variation of central metal atoms and counter ions. However conducting salts of bis(dithiolene) metal complexes show a tendency to form one-dimensional structures and become insulating at low temperatures although some superconductors have been discovered from $[M(dmit)_2]$ complexes (dmit = 4,5-disulfanyl-1,3-dithiole-2-thione).[2] Recently, it has been reported that the radical cation salts of $[M(dddt)_2]$ complexes (M = Ni, Pd; dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) produce various highly conducting salts metallic down to low temperatures.[3] $[M(dddt)_2]$ complexes were first synthesized about ten years ago[4] and have structures remarkably similar to that of the BEDT-TTF molecule. In this context, development of selenium analogues of $[M(dddt)_2]$ has attracted our interest because the selenium substitution of inner sulfur atoms is expected to increase the transverse interaction and to stabilize the metallic state at low temperature. This strong stabilization of the metallic state has been shown in BETS [bis(ethylenedithio)tetraselenafulvalene], the selenium analogue of BEDT-TTF, from which new organic superconductors have been recently discovered.[5] Here, we report on the synthesis, structure and physical properties of the new selenium containing metal complex $NBu_4[Ni(ddds)_2]$ **1**.

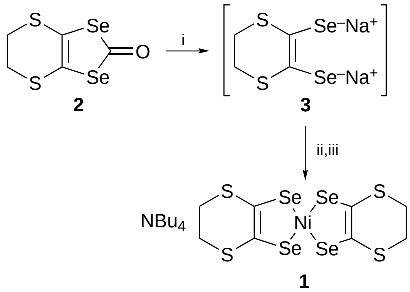
$NBu_4[Ni(ddds)_2]$ was synthesized as shown in Scheme 1. Ketone **2**[6] was hydrolysed with 20% sodium ethoxide in dry thf at 0 °C to generate the corresponding diselenolate **3**, which was treated successively with an ethanol solution of nickel dichloride hexahydrate and tetrabutylammonium bromide to crystallize the tetrabutylammonium nickel complex. The resultant precipitate was collected and washed with methanol and recrystallized from acetone–isopropyl alcohol to afford dark green and air-stable platelike crystals in 84% yield.†

The crystal structure‡ of the present complex is different from each of reported structures of $NBu_4[Ni(dddt)_2]$.[4c,d] In the unit cell there is one crystallographically independent tetrabutylammonium cation and a $[Ni(ddds)_2]$ anion. The molecular structure of the $[Ni(ddds)_2]$ anion is shown in Fig. 1. The nickel is coordinated by the four selenium atoms of the ligands in a slightly distorted square planar geometry with a dihedral angle of 15.7° between two five-membered rings. Each of the two chelating ligands is almost planar except for the ethylene bridge. The mean Ni–Se distance in the present anion [2.267(3) Å] is longer than that of the corresponding $[Ni(dddt)_2]$ anion [2.132(9) Å][4c] and the difference between these values (*ca.* 0.14 Å) is almost equal to that between the atomic covalent radii of sulfur and selenium. The intramolecular Se···Se lengths [Se(1)···Se(2) 3.268(3), Se(3)···Se(4) 3.267(3) Å] are longer than that of inner sulfur atoms of $[Ni(dddt)_2]^-$ [3.068(3) Å][4a] and are closer to the S···S lengths [S(1)···S(2) 3.451(8), S(3)···S(4) 3.461(7) Å]. This result suggests that the expanse of electron clouds of chalcogen atoms is nearly uniform in the transverse direction over the whole anion, in contrast to the case of $[Ni(dddt)_2]^-$, and therefore more effective two-dimensional intermolecular interaction is expected in its conducting solids. Fig. 2 shows the *bc*-projection for $NBu_4[Ni(ddds)_2]$ from which it is seen that there is no stacking or columnar structure of the anions and each anion is surrounded by counter tetrabutylammonium cations.



X = S; $[Ni(dddt)_2]^-$
X=Se; $[Ni(ddds)_2]^-$ **1**

Electrochemical properties were investigated by cyclic voltammetry. $NBu_4[Ni(ddds)_2]$ shows two pairs of reversible



Scheme 1 *Reagents and conditions*: i, 20% NaOEt (4 equiv.), thf, 0 °C, 2 h; ii, $NiCl_2 \cdot 6H_2O$ (0.5 equiv.) in EtOH, 0 °C, 2 h; iii, NBu_4Br (0.5 equiv.) in EtOH, 0 °C, 1 h

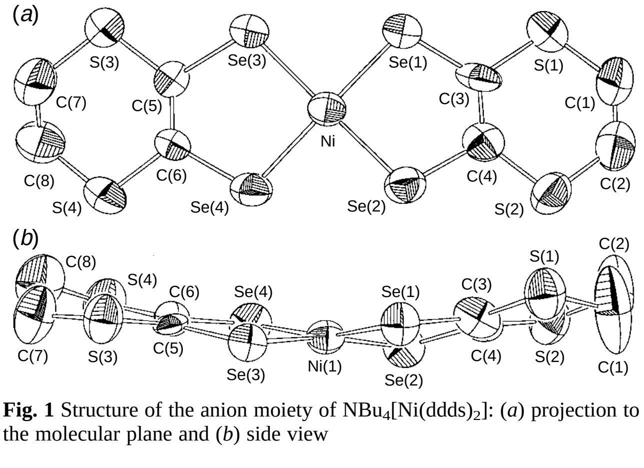


Fig. 1 Structure of the anion moiety of $NBu_4[Ni(ddds)_2]$: (*a*) projection to the molecular plane and (*b*) side view

redox waves, which correspond to the two redox processes leading the dianion to the neutral state, and one irreversible redox wave. The redox potentials of **1** and its related nickel dithiolene complexes are listed in Table 1. The first and second redox potentials are at −0.60 and +0.16 V, respectively, and are about 0.1 V higher than those of the sulfur derivative $NBu_4[Ni(dddt)_2]$ (−0.71 and +0.03 V) under identical conditions, suggesting that selenium lowers the electron-donating ability of **1**. On the other hand **1** shows an oxidation wave corresponding to the neutral to cationic state, although it is irreversible, suggesting the possibility of formation of radical cation salts of $[Ni(ddds)_2]$ similar to the case found for $[Ni(dddt)_2]$.

The room-temperature magnetic susceptibility of **1** was measured using a SQUID magnetometer at 1 T. Complex **1** is paramagnetic with $\mu_{eff} = 1.77\ \mu_B$ corresponding to one unpaired electron per molecular formula (calculated $\mu_{eff} = 1.73\ \mu_B$ for a one unpaired electron system) as a consequence of the crystal structure in which each anion is efficiently separated from others by bulky tetrabutylammonium cations, so preventing interaction.

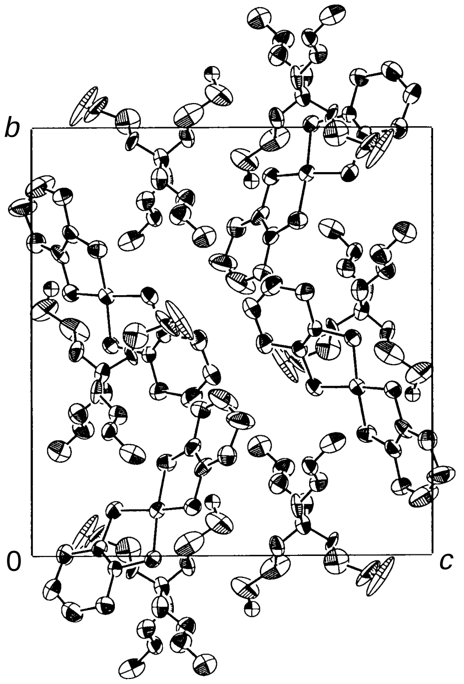


Fig. 2 Crystal structure of $NBu_4[Ni(ddds)_2]$ viewed along the *bc*-plane

Table 1 Redox potentials of **1** and related nickel dithiolene complexes[a]

$[ML_2]$[b]	$[ML_2]^{2-}$– $[ML_2]^-$	$[ML_2]^-$ $[ML_2]^0$	$[ML_2]^0$– $[ML_2]^{x}$[c]
$[Ni(ddds)_2]$	−0.60	+0.16	+0.71[d]
$[Ni(dddt)_2]$	−0.71	+0.03	+0.99[d]
$[Ni(dmit)_2]$	−0.18	+0.38	
$[Ni(mnt)_2]$[e]	+0.21	+1.19[d]	

[a] NBu_4PF_6 0.1 m in PhCN, Pt electrode, 20 °C, scan rate 200 mV s^{-1}, V *vs.* Ag/AgCl. [b] Tetrabutylammonium salt. [c] Oxidation state not clear. [d] Irreversible process with anodic peak potential quoted. [e] mnt = maleonitriledithiolate.

Synthesis of $[M(ddds)_2]^-$ complexes with other central metal atoms and preparation of their neutral species and conducting salts are now in progress.

Footnotes

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† ^1H NMR (270 MHz, $[^2H_6]$acetone) δ 3.31 (8 H, m), 1.90 (8 H, m), 1.56 (8 H, m), 1.30 (8 H, m) and 1.07 (12 H, m); IR (KBr) ν/cm^{-1} 2954m, 2866m, 1408s, 1282m, 1166w and 918w.

‡ *Crystal data* for $NBu_4[Ni(ddds)_2]$: $C_{24}H_{44}NNiS_4Se_4$, $M = 849.40$, monoclinic, space group $P2_1/c$, $a = 9.668(5)$, $b = 19.260(3)$, $c = 18.099(2)$ Å, $\beta = 97.87(2)°$, $U = 3338(1)$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}. Data collection was performed on a Rigaku AFC-5R diffractometer at 293 K equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,69$ Å) and rotating anode generator. Intensities were collected to a maximum 2θ value of 55.0° by the ω–2θ scan technique. The total number of independent reflections measured was 7698, of which 2359 were considered to be observed [$I > 3.00\sigma(I)$]. The structure was solved by direct methods (SHELXS-86). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The structure was refined by full-matrix least squares to $R = 0.065$, $R_w = 0.054$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/408.

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