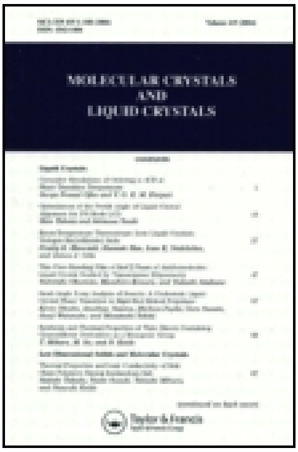

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Synthesis and Properties of Selenium Containing dmit-type Complexes

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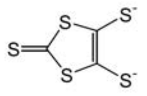
Four selenium containing dmit-type ligands (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) possessing 1,3-diselenole substructure, namely dmist (1,3-diselenole-2-thione-4,5-dithiolate), dsist (1,3-diselenole-2-thione-4,5-diselenolate), dmis (1,3-diselenole-2-selone-4,5-dithiolate), and dsis (1,3-diselenole-2-selone-4,5-diselenolate), and their nickel complexes were synthesized and characterized. The synthesis of the ligands involved lithiation reaction of 1,3-diselenole-2-selone as a key step followed by introduction of additional chalcogen atoms. The molecular structures of (n-Bu_4N)[Ni(dmist)$_2$], (n-Bu_4N)[Ni(dsist)$_2$], and (n-Bu_4N)[Ni(dsis)$_2$] were investigated by means of X-ray analyses, and a systematic enlargement of the anion size with the number of the introduced selenium atoms was revealed.

Keywords: metal complex; selenium atom; new ligands; X-ray crystallographic analysis

INTRODUCTION

Although most of molecular conductors currently studied are charge-transfer salts of TTF (tetrathiafulvalene)-type electron donors, the metal complexes of M(dmit)$_2$-type (M = Ni, Pt; dmit = 1,3-dithiole-2-thione-4,5-dithiolate) have occupied an important position in the development of molecular conductors and superconductors[1]. In the M(dmit)$_2$-type complexes, eight superconductors including α'-(EDT-TTF)[Pd(dmit)$_2$]$_2$ with the highest T_c = 6.5 K in this class[2], have been reported to date. However, most of them require application of high pressure to become superconductors and only one ambient pressure superconductor of this class, α-(EDT-TTF)[Ni(dmit)$_2$]$_2$, has been known[3]. In this respect, introduction of selenium atoms instead of sulfur atoms in the dmit ligand is particularly interesting in order to enhance the intermolecular interaction and the dimensionality of the resulting metal complexes. Thus, the syntheses of metal complexes with dsit (1,3-dithiole-2-thione-4,5-diselenolate) [4], dmise (1,3-dithiole-2-selone-4,5-dithiolate)[5], dsise (1,3-dithiole-2-selone-4,5-diselenolate)[6], and dsis (1,3-diselenole-2-selone-4,5-diselenolate)[7] have been investigated. Of them, dsis, long known since 1976, is the only one ligand having a 1,3-diselenole moiety, and no other ligands with 1,3-diselenole moiety, such as dmis (1,3-diselenole-2-selone-4,5-dithiolate), dsist (1,3-diselenole-2-thione-4,5-diselenolate), and dmist (1,3-diselenole-2-thione -4,5-dithiolate) have been so far unknown, although they are very interesting as potential components for molecular conductors and superconductors.

On our way to develop new TSF (tetraselenafulvalene)-type electron donors, we established several useful reactions for synthesizing selenium containing ring systems[8,9], and the application of these reactions has made it possible to synthesize dmis, dsist, and dmist. In this paper, we describe the synthesis of these new ligands and their nickel complexes, together with the crystal structures of the nickel complexes.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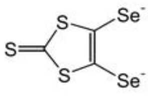
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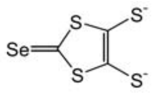
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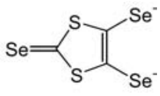
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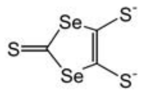
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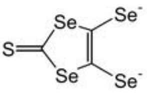
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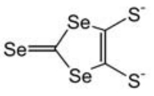
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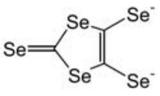
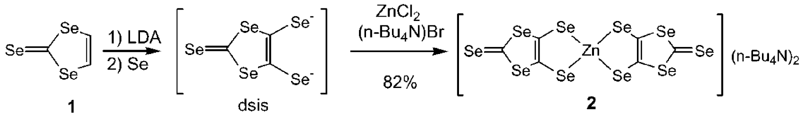

dsis

RESULTS AND DISCUSSION

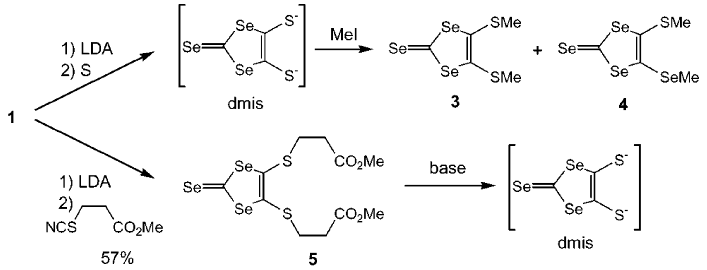
Synthesis

We have recently reported an effective synthetic method of dsis via lithiation of 1,3-diselenole-2-selone (**1**) [8], which was isolated as a zincate complex (Scheme 1) [10].



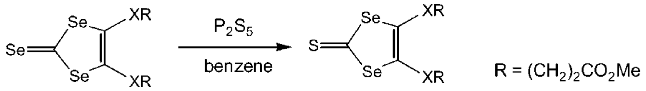
SCHEME 1 Effective synthesis of dsis and its zinc complex[10].

With the same strategy, the synthesis of dmis was attempted by a reaction of dilithiated 1,3-diselenole-2-selone (**1**) with elemental sulfur as shown in Scheme 2. The analysis of the product after alkylation, however, indicated that the expected product, 4,5-dimethylthio-1,3-diselenole-2-selone (**3**) was heavily contaminated (up to 20%) with byproduct possessing the methylseleno moiety (**4**). Since it was practically impossible to remove **4**, we pursued an alternative route to synthesize pure dmis and found that a reaction of the dilithio intermediate with 3-thiocyanatopropionic acid methyl ester[9,11] gave 4,5-bis(2-methoxycarbonylethylthio)-1,3-diselenole-2-selone (**5**) in 57% isolated yield. The 2-methoxycarbonylethyl groups in compound **5** can be removed by an action of strong base to in situ produce dmis[11,12]. Thus **5** is a synthetic equivalent of dmis, and it should be noted that 3-thiocyanetopropionic acid methyl ester acts two roles in this synthesis, i.e. introduction of sulfur atom as well as the protecting group for thiolate moiety at the same time.



SCHEME 2 Synthesis of dmis via lithiation of 1,3-diselenole-2-selone.

For the synthesis of dmist and dsist possessing the 1,3-diselenole-2-thione substructure, transchalcogenation reaction from selenocarbonyl to thiocarbonyl moiety at the stage of the protected dmis (**5**) and dsis (**6**) [10] was examined with a reactive sulfurization reagent P_2S_5 as shown in Scheme 3. The desired 1,3-diselenole-2-thione derivatives (**7** and **8**) were obtained in 64% and 52% isolated yields respectively.

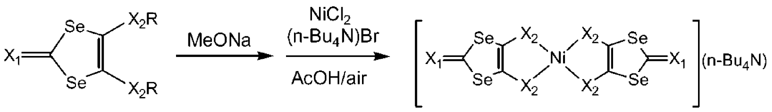


5 X = S
6 X = Se

7 X = S (64%)
8 X = Se (52%)

SCHEME 3 Transchalcogenation reaction from the selones to thiones.

Treatment of the precursors (**5–8**) with sodium methoxide in methanol, in situ generating the free dithiolate or diselenolate ligands, followed by a reaction with $NiCl_2$ in the presence of tetrabutylammonium bromide afforded the nickel complexes (**9–12**) as shown in Scheme 4[12].



5- 8

	X_1	X_2	yield/%
9	S	S	69
10	S	Se	57
11	Se	S	69
12	Se	Se	43

SCHEME 4 Synthesis of nickel complexes (**9–12**).

Crystal structures

Recrsytalliztion of the nickel complexes from acetone–methanol under nitrogen atmosphere gave black needles of sufficient quality for X-ray crystallographic analysis in case of $(n\text{-}Bu_4N)[Ni(dmist)_2]$ (**9**), $(n\text{-}Bu_4N)[Ni(dsist)_2]$ (**11**), and $(n\text{-}Bu_4N)[Ni(dsis)_2]$ (**12**) [13]. As seen in many $[M(dmit)_2]$ type anions, all the present anions have almost completely flat structures. The anion part of **11** is shown in Figure 1 as a representative. In order to compare the size of the anions, the distances (d_1 and d_2) between chalogen atoms are summarized in Table 1 together with those of $(n\text{-}Bu_4N)[Ni(dmit)_2]$. As expected, the introduction of selenium atoms systematically enlarges the size of the anion. It should be noted that the difference between d_1 and d_2 reduces in the following order; $[Ni(dmit)_2]^{-1}$ (0.24 Å) > $[Ni(dsist)_2]^{-1}$ ≈ $[Ni(dsis)_2]^{-1}$ (~ 0.20 Å) > $[Ni(dmist)_2]^{-1}$ (0.12 Å). The shape of $[Ni(dmist)_2]^{-1}$ anion is close to a rectangle, which is fairly different from that of $[Ni(dmit)_2]^{-1}$, in which the central sulfur atoms protruded to the molecular circumference. This means that the shape of the anion is tunable by the combination of chalcogen atoms, which would be influential in the packing pattern as well as intermolecular interaction in the solid state. Considering both the anion shape and the coefficient distribution in the frontier orbitals, the present selenium containing ligands will provide a tool to control the electronic structure of conductive molecular solids of this class.

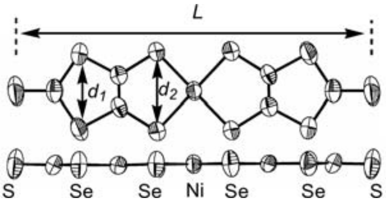


FIGURE 1 Structure of $[Ni(dsist)_2]^{-1}$; the distances between chalcogen atoms are given in TABLE 1.

TABLE 1 Selected chalcogen – chalcogen distances in the Ni complexes

	d_1 /Å	d_2/Å	L/Å
$[Ni(dmist)_2]^-$	3.08	3.20	14.57
$[Ni(dsist)_2]^-$	3.11	3.30	14.96
$[Ni(dsis)_2]^-$	3.11	3.31	15.26
$[Ni(dmit)_2]^-$	2.88	3.12	14.22

CONCLUSION

We have established the effective syntheses of new selenium containing ligands including dmist, dmis, and dsist, together with their nickel complexes. The synthesis of the ligands involves lithiation of 1,3-diselenole-2-selone followed by introduction of chalcogen atoms as a key step. In addition, transchalcogenation reaction from the selone to thione moiety is successfully achieved by use of P_2S_5 in acceptable yields. The X-ray structural analyses of the nickel complexes indicate that the anion shape and size are systematically altered by the introduction of selenium atoms. This will give an opportunity to control the electronic structures as well as solid state properties of conductive molecular solid based on $M(dmit)_2$-type metal complexes.

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[12.] All new compounds were characterized by elemental analyses and NMR, IR and MS spectroscopy. Selected physical and spectral data. (n-Bu$_4$N)[Ni(dmist)$_2$] (**9**): black needles from acetone–methanol (1:1, v/v); mp 175–177 °C (melt with decomposition); MS (MALDI-TOF) m/z 639 (M^-–n-Bu$_4$N); Anal. Calcd for $C_{22}H_{36}NS_6Se_4Ni$: C, 29.98; H, 4.12; N, 1.59%. Found: C, 29.81; H, 4.13; N, 1.65%. (n-Bu$_4$N)[Ni(dmis)$_2$] (**10**): black needles from acetone–methanol (1:1, v/v); mp 180–184 °C (melt with decomposition); MS (MALDI-TOF) m/z 827 (M^-–n-Bu$_4$N); Anal. Calcd for $C_{22}H_{36}NS_2Se_8Ni$: C, 24.72; H, 3.39; N, 1.31%. Found: C, 24.55; H, 3.51; N, 1.32%. (n-Bu$_4$N)[Ni(dsist)$_2$] (**11**): black needles from acetone–methanol (1:1, v/v); mp 153–157 °C (melt with decomposition); MS (MALDI-TOF) m/z 734 (M^-–n-Bu$_4$N); Anal. Calcd for $C_{22}H_{36}NS_4Se_6Ni$: C, 27.09; H, 3.72; N, 1.44%. Found: C, 26.33; H, 3.76; N, 1.44%. (n-Bu$_4$N)[Ni(dsis)$_2$] (**12**): black needles from acetone–methanol (1:1, v/v); mp 171–173 °C (melt with decomposition, ref 164–168 °C [7]); Anal. Calcd for $C_{22}H_{36}NSe_{10}Ni$: C, 22.72; H, 3.12; N, 1.21%. Found: C, 22.68; H, 3.04; N, 1.18%.

[13.] Crystal data for (n-Bu$_4$N)[Ni(dmist)$_2$]: $C_{22}H_{36}NS_6Se_4Ni$, M = 881.43, *monoclinic*, space group $C2/c$, a = 20.532(1), b = 13.5430(7), c = 12.1548(8) Å, β = 105.854(2)°, V = 3251.3(3) Å^3, Z = 4, D_c = 1.80 g cm^{-3}, R = 0.095, R_w = 0.110 for 1283 observed reflections [I>3.0 σ (I)]. Crystal data for (n-Bu$_4$N)[Ni(dsist)$_2$]: $C_{22}H_{36}NS_2Se_8Ni$, M = 1069.03, *monoclinic*, space group $C2/c$, a = 20.806(2), b = 13.673(3), c = 12.248(3) Å, β = 105.65(1)°, V = 3355(1) Å^3, Z = 4, D_c = 2.12 g cm^{-3}, R = 0.039, R_w = 0.036 for 1349 observed reflections [I>3.0 σ (I)]. Crystal data for (n-Bu$_4$N)[Ni(dsis)$_2$]: $C_{22}H_{36}NSe_{10}Ni$, M = 1162.83, *monoclinic*, space group $P2_1/a$, a = 12.384(7), b = 13.529(4), c = 21.098(3) Å, β = 106.18(2)°, V = 3394(2) Å^3, Z = 4, D_c = 2.28 g cm^{-3}, R = 0.043, R_w = 0.037 for 2555 observed reflections [I>3.0 σ (I)].