

An Improved Synthesis of Nickel-bis[5,6-dihydro-1,4-dioxine-2,3-dithiolate], Ni(edo)₂

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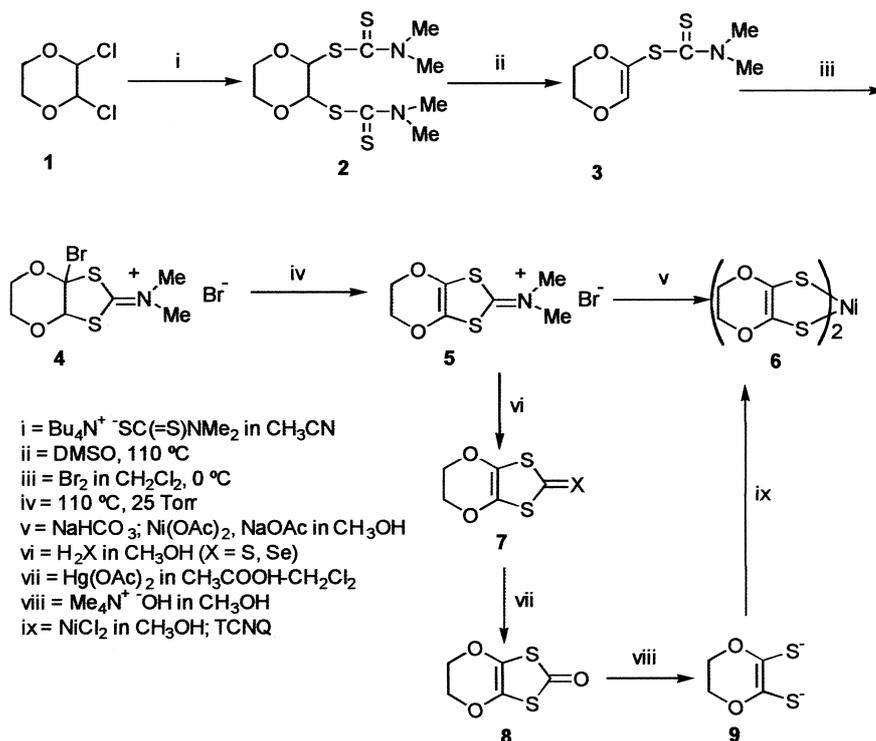
Starting from 2,3-dichloro-1,4-dioxane, the title compound was prepared by a five-step chemical procedure, instead of a eight-step procedure reported recently.

Recently, a novel donor-type metal 1,2-dithiolene complex, Ni(edo)₂ [edo = 5,6-dihydro-1,4-dioxine-2,3-dithiolate] (**6**) and its mixed-ligand de-

rivatives have been synthesized and characterized [1]. According to the literature [1–3] and starting from 2,3-dichloro-1,4-dioxane (**1**), an eight-step procedure has been employed to achieve the required compound **6** via the intermediate 4,5-ethylenedioxy-1,3-dithiol-2-one (**8**).

In this paper, a shorter (five-step) procedure is described in which the intermediate 4,5-ethylenedioxy-2-(*N,N*-dimethylamino)-1,3-dithiolium bromide (**5**) [2–4] is converted directly, in one synthetic operation, into the nickel complex **6**. A similar procedure has been applied for the preparation of some metal 1,2-diselenolates from the corresponding 2-(*N,N*-dialkylamino)-1,3-diselenolium salts [5]. The two alternative (eight-step and five-step) procedures are outlined in Scheme 1.

It was found that the analytical and spectroscopic data of Ni(edo)₂ obtained by the five-step procedure are identical with those obtained for the product prepared by the eight-step procedure [1]. In the eight-step procedure the intermediate **8** has been obtained in a yield of 35% based on **2** [2, 3], and the required compound **6** in a maximum yield of 54% based on **8** [1, 2] or 19% based on **2**. In other words, the yield from the five-step pro-



Scheme 1.

cedure is higher than that of the eight-step procedure. Moreover, the toxic reagents H_2Se (or H_2S) and $\text{Hg}(\text{OAc})_2$, as well as tetracyanoquinodimethane (TCNQ), used in the earlier procedure, were avoided in our procedure. However, some trial experiments under several conditions are required to optimize the yield in the five-step procedure. The new method is suggested for the preparation of similar compounds such as $\text{Ni}(\text{dodt})_2$ [dodt = 5,6-dihydro-1,4-oxathiine-2,3-dithiolate], $\text{Ni}(\text{ddots})_2$ [ddots = 5,6-dihydro-1,4-dioxine-2,3-thioselenolate], and $\text{Ni}(\text{ddsts})_2$ [ddsts = 5,6-dihydro-1,4-diothiine-2,3-thioselenolate], using the corresponding *N,N*-dialkylamminium salts, reported in [6], [7] and [8], respectively.

Experimental Section

Details on the preparation of the intermediate material **4** from **1** are reported in [2] (see also [3]). This compound (732 mg, 2 mmol) was pyrolyzed at 110 °C under reduced pressure (25 Torr) for

2–3 h to give **5**. Then, NaHCO_3 (288 mg, 4 mmol) and a solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (250 mg, 1 mmol) and CH_3COONa (328 mg, 4 mmol) in degassed cooled (0 °C) CH_3OH (30 ml) was added to the freshly prepared compound **5** with stirring under Ar atmosphere. After stirring for 0.5 h at 0 °C and 0.5 h at r.t., the mixture (solution and precipitate) was evaporated to dryness and extracted with CH_2Cl_2 . Purification by silica gel column chromatography, using CH_2Cl_2 as eluent, afforded from the first fraction 100 mg of **6** (yield 28% based on **4**). Recrystallization from CH_2Cl_2 –PrOH gave deep blue plates. A solution of $\text{Ni}(\text{edo})_2$ in CH_2Cl_2 has a blue-green color and exhibits a strong optical absorption band at 853 nm. – $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}_4\text{Ni}$ (355.104); calcd. C 27.06, H 2.27, S 36.12; found C 27.11, H 2.23, S 36.02.

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