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 an 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 derivatives 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-
procedure is higher than that of the eight-step procedure. Moreover, the toxic reagents \( \text{H}_2\text{Se} \) (or \( \text{H}_2\text{S} \)) and \( \text{Hg}()\text{(OAc)}_2 \), as well as tetracyanoquinodimethane (TCNO), 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 \( \text{Ni}(\text{dodt})_2 \) \( \text{dodt} = \text{5,6-dihydro-1,4-oxathiine-2,3-dithiolate} \), \( \text{Ni}(\text{ddots})_2 \) \( \text{ddots} = \text{5,6-dihydro-1,4-dioxine-2,3-thioselenolate} \), and \( \text{Ni}(\text{ddsts})_2 \) \( \text{ddsts} = \text{5,6-dihydro-1,4-dithiole-2,3-thioselenolate} \), using the corresponding \( \text{N},\text{N}-\text{dialkylaminium} \) 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, \( \text{NaHCO}_3 \) (288 mg, 4 mmol) and a solution of \( \text{Ni(OAc)}_2 \cdot 4\text{H}_2\text{O} \) (250 mg, 1 mmol) and \( \text{CH}_3\text{COONa} \) (328 mg, 4 mmol) in degassed cooled (0 °C) \( \text{CH}_3\text{OH} \) (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 \( \text{CH}_3\text{Cl}_2 \). Purification by silica gel column chromatography, using \( \text{CH}_3\text{Cl}_2 \) as eluent, afforded from the first fraction 100 mg of 6 (yield 28% based on 4). Recrystallization from \( \text{CH}_3\text{Cl}_2 \cdot \text{PrOH} \) gave deep blue plates. A solution of \( \text{Ni(edo)}_2 \) in \( \text{CH}_3\text{Cl}_2 \) 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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