Alternative Method for the Preparation of Ni(dddt)(edt) (dddt = 5,6-Dihydro-1,4-dithiin-2,3-dithiolate, edt = cis-1,2-Ethylenedithiolate) and Similar Complexes

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Starting from 4,5-(ethylenedithio)-1,3-dithiol-2-one and 1,3-dithiol-2-one the disodium 5,6-dihydro-1,4-dithiin-2,3-dithiolate (Na2dddt) and disodium 1,2-dithiolate (Na2edt) salts were prepared, which react with NiCl2 in air to give the complex Ni(dddt)(edt) (3ab). This compound was characterized analytically and spectroscopically. The method is applicable for the preparation of similar unsymmetrical complexes.

Key words: Metal 1,2-Dithienolens, π-Donor Molecules, Organic Conductors

Introduction

During the last fifteen years, a large number of conducting materials based on metal 1,2-dithiolenes and selenium analogs have been prepared and studied. For some review articles of the published papers, see [1 – 3]. The metal 1,2-dithiolene complexes were prepared in several forms i.e., dianionic, monoanionic, fractional anionic, neutral, and fractional cationic. The fractional anionic (cation deficient) and/or neutral complexes were obtained by oxidation of the anionic complexes with agents, like tetracyanoquinodimethane (TCNQ), or by electrooxidation [4, 5]. Most of the known complexes are symmetrical (i.e., have a single ligand). Only a limited number of unsymmetrical (i.e., mixed ligand) complexes are known [3, 4, 6, 7]. The unsymmetrical complexes have been prepared from the corresponding symmetrical ones, mainly, by ligand-exchange reactions in solvents at reflux temperature [4, 6, 7]. However, some complexes are decomposed under these conditions. For example, Ni(edt)2 (where edt is the ligand cis-1,2-ethylenedithiolate) undergoes extensive decomposition during attempts of recrystallization from higher boiling solvents [8]. This means that e.g., the ligand exchange reaction between Ni(edt)2 and Ni(dddt)2 (where dddt is the ligand 5,6-dihydro-1,4-dithiin-2,3-dithiolate) [9] to form Ni(dddt)(edt) in refluxing 1,2-dichloroethane is not possible. We found that the ligand exchange reaction of saturated solutions of (Bu4N)Ni(edt)2 with Ni(dddt)2 in 1,2-dichloroethane at ca. 60 °C gave only traces of Ni(dddt)(edt) after one month [10].

In this paper, the preparation of Ni(dddt)(edt) at low temperatures is described. The chemical procedure is indicated in Scheme 1.

The starting materials, 4,5-(ethylenedithio)-1,3-dithiol-2-one (1a) and 1,3-dithiol-2-one (1b), react with sodium methoxide in MeOH to give the salts Na2dddt (2a) and Na2edt (2b), respectively. Mixture of these salts react with NiCl2 in air to give the required unsymmetrical complex Ni(dddt)(edt), i.e., 3ab and the corresponding symmetrical ones Ni(dddt)2 (3aa) and Ni(edt)2 (3bb). Also, one can use the corresponding organotin thiolates 4a and 4b [11, 12], instead of sodium dithiolate salts. The method could be applied for the preparation of similar complexes.
Results and Discussion

By the method described herein the unsymmetrical complex Ni(dddt)(edt) was obtained in acceptable yield (5.5%), considering that the ligand exchange method can not be applied for the preparation of this complex. It is similar to the cross coupling method, applied for the preparation of unsymmetrical tetrathiafulvalenes (TTFs) [2, 13]. Near IR spectroscopic investigation indicated the formation of anionic species, i.e., NaNi(dddt)₂, NaNi(edt)₂, NaNi(dddt)(edt) as intermediates which are soluble in MeOH. These are oxidized in air to give the neutral complexes. Fig. 1 shows that the UV-vis/near IR optical absorption spectrum of 3ab in MeOH and the spectra of 3aa and 3bb for comparison. The absorption peaks of the unsymmetrical complex Ni(dddt)(edt) occur between the peak positions of the corresponding symmetrical complexes, Ni(dddt)₂ (3aa) and Ni(edt)₂ (3bb), as in the case of unsymmetrical and symmetrical TTFs [2, 13]. The low frequency bands at λ_max = 864, 1015 and 719 nm are characteristic of metal 1,2-dithiolene complexes. For spectroscopic studies of 3aa and 3bb see also [8, 14, 15]. It is expected that the redox potentials of Ni(dddt)(edt) will have intermediate values, i.e., in between the redox potential values of Ni(dddt)₂ and Ni(edt)₂ as in the case of other metal 1,2-dithiolenes [3, 4] and TTFs [2, 13]. This means that the donor ability of Ni(dddt)(edt) will be better than that of Ni(dddt)₂.

The method described herein was also applied for the preparation of Pd(dddt)(edt) (λ_max = 875 nm in CH₃CN) and Ni(dt)(edt) (where dt is the ligand tetra-thiafulvalene-dithiolate [16, 17]) (λ_max = 830 nm in CH₂CN). The method is general and can be applied for the preparation of a wide variety of unsymmetrical metal 1,2-dithiolenes based on several transition metals with small [2, 3, 13] and large (i.e., extended-TTF) [17] dithiolate ligands, as well as with the selenium analogs. However, details on the preparation and properties of the new unsymmetrical complexes will be published elsewhere.

Experimental Section

The starting materials 1a and 1b were prepared by the well known chemical procedures (see [2, 11 – 13]).

Fig. 1. UV-vis/near IR optical absorption spectra of Ni(dddt)₂ (a), Ni(edt)₂ (b) and Ni(dddt)(edt) (c) in MeOH.
[6] G. A. Mousdis, N. Assimomytis, G. C. Anyfantis, G. C. Papavassiliou, unpublished work concerning symmetrical and unsymmetrical Ni-complexes with 5,6-dihydro-6-methyl-1,4-dithiin-2,3-dithiolate and 5,6-dihydro-5,6-dimethyl-1,4-dithiin-2,3-dithiolate ligands.