



Synthesis, experimental and theoretical investigation of a new type nickel dithiolene complex



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ABSTRACT

A new nickel complex with an extended multisulfur dithiolene ligand, [Ni(dmeodddt)₂] (dmeodddt = 5,6-dimethoxy-5,6-dihydro-1,4-dithiine-2,3-dithiolate), has been synthesized and characterized by IR, Raman, UV–Vis and NMR spectroscopy. Its crystal structure has been determined by X-ray crystallography, showing that the Ni atom is tetra-coordinated and has a square planar geometry with the methoxy groups placed above and below the metal dithiolene core, due to stereochemical hindrance. Electrochemical measurements showed that the complex exhibits four 1e[−] reversible redox waves. The results of theoretical calculations showed a good agreement with the experimental findings and gave answers about its electronic structure.

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1. Introduction

Metal 1,2-dithiolenes have been widely studied during the past few decades. The intense interest in dithiolene complexes is the result of both their intrinsic interest and their applications as molecular materials with conducting [1,2], magnetic [3], optical [4–6] and other properties due to their unique electronic structures [7–11]. The electronic, optical and magnetic properties of these materials can be tuned through modification of the organic dithiolene ligands [12]. In addition to such tuning at the molecular level, the bulk properties can also be tuned via crystal engineering as the strong intermolecular interactions arising from the large number of sulfur and other heavy atoms in these complexes allows a wide variety of 3-D crystalline structures [13].

Complexes of [Ni(dmit)₂]^{n−}, [(dmit) = 1,3-dithiol-2-thione-4,5-dithiolate] were found to be molecular conductors and superconductors [14]. This prompted many laboratories to explore new complexes in this area [15]. One of the most widely studied dithiolene ligands for the preparation of metal complexes has been dddt [dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate]. This ligand is the inorganic structural analog to fragments of BEDT-TTF (bis ethylenedithio tetrathiafulvalene), that gave many conducting radical salts, some of which with superconducting properties. A detailed

analysis of a number of metal complexes with this ligand, [M(dddt)₂] (M = Ni, Pd, Pt, Cu, Au, Co), has been reported [16].

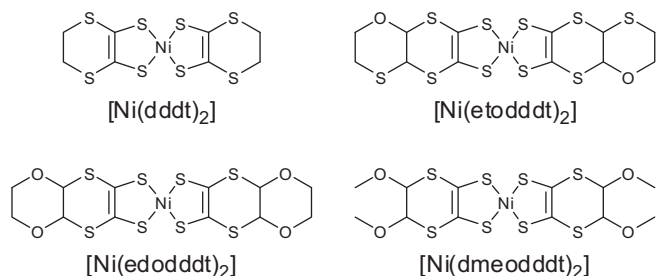
One approach to maximizing electron delocalization in the organic ligand is through the fusion of organic rings onto the square planar metal dithiolene core [17], thus increasing the size and enhancing orbital overlap, giving them peculiar molecular properties such as high thermal and photochemical stabilities and intense vis-near-IR absorption [17]. This approach should allow elaborate systems to be developed with highly tuneable electronic structures and solid state arrangements. It is difficult to predict which structural changes to a ligand produce significant stereo-electronic differences in the metal complexes. For that reason, a number of metal-bis-1,2-dithiolene complexes with SR groups attached at the periphery were synthesized and studied [9].

In our previous work we synthesized and studied dddt analogues by extending the outer rings, either with an ethylene thioxo- group, leading to [Ni(etodddt)₂] [etodddt = 2,3,4a,8a-tetrahydro-[1,4]dithiino[2,3-b][1,4]oxathiine-6,7-dithiolate] [18], or with an ethylene dioxo- group, leading to [Ni(edodddt)₂] [edodddt = 2,3,4a,8a-tetrahydro-[1,4]dithiino[2,3-b][1,4]dioxine-6,7-dithiolate] [4]. In both works the role of the external ligand unit on the molecular structure and crystal packing was discussed.

In continuation of this work and for an investigation into the electronic and structural effects of substitution on the external ligand unit of dddt, a new metal 1,2-dithiolene compound, containing two methoxy groups as an extension, was synthesized, namely

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Scheme 1. Structural formulas of $[\text{Ni}(\text{dmeodddt})_2]$, $[\text{Ni}(\text{edodddt})_2]$, $[\text{Ni}(\text{etodddt})_2]$ and $[\text{Ni}(\text{dddtd})_2]$.

$[\text{Ni}(\text{dmeodddt})_2]$. Electrochemical and X-ray measurements and spectral investigations have been made. These measurements were also compared to those of the compounds $[\text{Ni}(\text{etodddt})_2]$ and $[\text{Ni}(\text{edodddt})_2]$. DFT studies of the new compound's structural, electronic, spectral and vibronic properties are also included.

The reason for choosing this group was because $[\text{Ni}(\text{dmeodddt})_2]$ [$\text{dmeodddt} = 5,6\text{-dimethoxy-5,6-dihydro-1,4-dithiine-2,3-dithiolate}$] looks similar to the compounds $[\text{Ni}(\text{edodddt})_2]$ and $[\text{Ni}(\text{etodddt})_2]$ (Scheme 1), but the MeO groups are not bonded together to form a ring, so there are more potential arrangements. Due to this we expect better solubility and maybe a different crystal packing.

2. Experimental

2.1. Materials and methods

$(\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ was prepared according to the literature [19]. All starting materials were of analytical grade, obtained commercially and used as received, except for methanol, which was dehydrated according to the literature [20]. Scheme 2 summarizes the synthetic procedure leading to $[\text{Ni}(\text{dmeodddt})_2]$.

2.2. Synthesis of 1,2-dichloro-1,2-dimethoxy ethane (1) [21]

9.60 g of glyoxal trimeric dihydrate (45.7 mmol) were dissolved in a mixture of 12.8 mL of methanol and 24.0 mL of carbon tetrachloride, with the addition of 1.0 mL of thionylchloride. The solution was cooled to 0°C and 23.0 mL of thionylchloride were added dropwise under stirring. After 30% of the SOCl_2 had been added, a vigorous gaseous evolution took place and the reaction became endothermic; the solution was then left to reach room temperature. The SOCl_2 was then added faster than before to keep the reaction temperature at $20\text{--}25^\circ\text{C}$, and if necessary the mixture was heated. The addition took about 6 hr. and the mixture was then stirred overnight at room temp. The solvent and excess SOCl_2 were evaporated under vacuum, and the residue distilled at 19–

20 Torr, to isolate the desired product in the liquid form at 79°C . It consists mainly of the *rac* and *meso* isomers, and when cooled to $0\text{--}4^\circ\text{C}$ crystals of the *meso* form were precipitated as a white solid.

Yield: 4.50 g (28.3 mmol), (20.6%), mp: 72°C (*meso* form); ^1H NMR (300 MHz, CDCl_3) δ (ppm): 5.49 and 5.56 (s, 2H *meso* and *rac*), 3.60 and 3.59 (s, 6H *meso* and *rac*); ^{13}C NMR (300 MHz, CDCl_3) δ (ppm): 97.36 and 97.20 (s, C–C *meso* and *rac*), 58.33 and 58.13 (s, CH_3 *meso* and *rac*);

2.3. Synthesis of 5,6-dimethoxy-5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione (2)

1,2-Dichloro-1,2-dimethoxy ethane (1) (1.59 g, 10.0 mmol) and 4.7 g (5.0 mmol) of $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{dmit})_2]$ were dissolved in 100 mL acetone. The solution was refluxed for 48 h and the color changed from bright red to yellow-brown. The solvent was evaporated under vacuum and the resulting dark-brown sticky residue was dissolved in 200 mL of dichloromethane and washed twice with 200 mL of water. The organic layer was dried with magnesium sulfate and condensed under vacuum to 10 mL. Purification of the final product was made by column chromatography in silica gel using CH_2Cl_2 as the eluent. Yellow-orange crystals were produced. Depending on the starting material, the product can consist of the *meso* isomer or a mixture of the *meso* and *rac* isomers. Yield: 1.4 g, (49%); mp: 130°C (*meso*); UV–Vis (CH_2Cl_2 , nm): 405, 272; ^1H NMR (300 MHz, CDCl_3) δ (ppm): 5.33 (s, 1H), 3.58 (s, 3H) for the *meso* form and 4.98 (s, 1H), 3.55 (s, 3H) for the *rac* form; IR data (ν , cm^{-1}): 2996, 2948, 2921, 2890, 2875, 2826, 1483, 1445, 1435, 1321, 1247, 1230, 1184, 1106, 1064, 1045, 1023, 968, 937, 887, 827, 724, 616.

2.4. Bis[5,6-dimethoxy-5,6-dihydro-1,4-dithiine-2,3-dithiolate] nickel tetramethylammonium $[(\text{Me}_4\text{N})\text{Ni}(\text{dmeodddt})_2]$ (3)

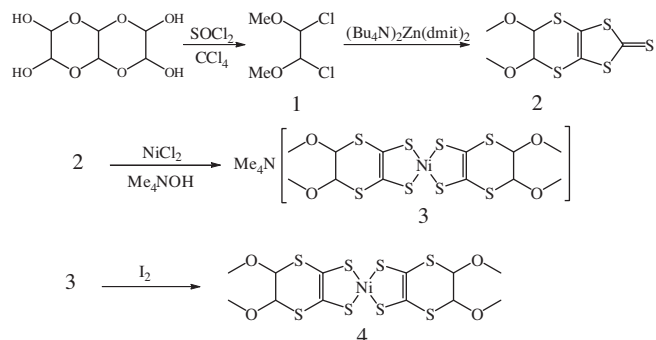
In a dispersion of thione 2 (200 mg, 0.70 mmol) (*meso* form) and nickel chloride hexahydrate (50 mg, 0.35 mmol) in 20 mL methanol under N_2 , 1 mL of hydroxyl tetramethylammonium, 25% in methanol was added. The mixture was stirred for 12 h, under a nitrogen atmosphere. The solid was removed by filtration in a vacuum and washed repeatedly with methanol to give 3 as a brown powder.

Yield: 165 mg, (77%) of pure product; mp: $>290^\circ\text{C}$; UV–Vis (CH_2Cl_2 , nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)): 1144 (25493), 603 (5259), 389 (18165), 317 (9114), 250 (95557); IR data (ν , cm^{-1}): 2957, 2929, 2871, 2824, 1479, 1457, 1366, 1320, 1223, 1185, 1151, 1106, 1092, 1027, 933, 856, 839, 737, 629; Elemental Anal. Calc. for $\text{C}_{16}\text{H}_{28}\text{NNiO}_4\text{S}_8$: C, 31.32; H, 4.60. Found: C, 31.65; H, 4.88%.

2.5. Bis[5,6-dimethoxy-5,6-dihydro-1,4-dithiine-2,3-dithiolate] nickel $[\text{Ni}(\text{dmeodddt})_2]$ (4)

Compound 3 (65 mg 0.11 mmol) was dissolved in acetonitrile (30 mL), heated and filtered. A solution of iodine (30 mg, 0.12 mmol) in acetonitrile (30 mL) was added to the filtrate. The mixture stirred for 40 min and left to stand at room temperature for 24 h to give dark green crystalline powder that was filtered and washed with acetonitrile.

Yield: 33 mg, (56%); mp: $>290^\circ\text{C}$; UV–Vis (CH_2Cl_2 , nm (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)): 986 (69650), 653 (2820), 366 (17872), 364 (18044), 311 (92133), 268 (66033); IR data (ν , cm^{-1}): 2993, 2956, 2927, 2894, 2874, 2852, 2831, 1450, 1344, 1315, 1259, 1239, 1207, 1182, 1112, 1072, 1022, 965, 941, 894, 817, 736, 721, 626; Raman Shifts (cm^{-1}): 150, 235, 275, 348, 368, 380, 414, 480, 542, 626, 911, 1023, 1244, 1342, 1355, 2833, 2933; δH (300 MHz, CDCl_3) δ (ppm): 5.18 (s, 2H), 3.59 (s, 6H); ^{13}C NMR (300 MHz, CDCl_3) δ (ppm):



Scheme 2. Synthetic route to the $[\text{Ni}(\text{dmeodddt})_2]$.

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