



Synthesis and characterization of a new series of nickel dithiolate compounds containing both acridinium cations and halogen anions



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ABSTRACT

A new class of $[\text{Ni}(\text{dmit})_2]^-$ compounds, $[\text{AcrH}][\text{Ni}(\text{dmit})_2][\text{MeOH}]$ (**1**), $[\text{AcrH}]_2[\text{Ni}(\text{dmit})_2][\text{Cl}]$ (**2**), $[\text{AcrH}]_2[\text{Ni}(\text{dmit})_2][\text{Br}]$ (**3**) (where AcrH represents protonated acridinium) have been synthesized. The as synthesized compounds were characterized by ESI-MS, IR, UV-Vis and X-ray crystallography. We show that small changes in the chemical composition of these salts lead to significant difference in their crystal structure and physical properties. As compared to compounds **2** and **3**, compound **1** exhibits better conductivity and stronger anti-ferromagnetic interaction owing to shorter S...S distances. Compound **1** can self-assemble into high crystalline rod-shape crystals due to the abundant inter-molecular interactions. Compounds **2** and **3** represent the first examples where the halogen anions are incorporated into the separated sheets of $\text{Ni}(\text{dmit})_2$ units.

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1. Introduction

Over the past several decades, π -planar metal coordination compounds, $[\text{Ni}(\text{dmit})_2]^{n-}$ ($\text{dmit}^{2-} = 2$ -thioxo-1,3-dithiole-4,5-dithiolate), has received extensive research interest due to its intriguing chemical and physical properties [1,2]. The nickel bis(dithiolene) complex in different oxidation states serve as a source of conducting electrons and/or localized $S = 1/2$ spins to derive electrically and/or magnetically active molecular materials [3–12]. In addition, the monovalent $[\text{Ni}(\text{dmit})_2]^-$ co-crystallize with various counter cations and radicals [13–29]. The π - π and sulfur-sulfur interactions are sensitive to the counter cations, resulting in various molecular arrangements that manipulate the electrical and/or magnetic properties of the complexes. It is of great importance to control the structure and property of ionic compounds containing $[\text{Ni}(\text{dmit})_2]^-$ through the selection of suitable cations.

Acridine and its derivatives belong to heterocyclic analogs of anthracene, with the central ring contain nitrogen instead of a carbon atom. The cations of acridine and its derivatives can be

obtained by protonation or methylation of the nitrogen atoms [30–32]. As compared to other non-planar counter cations such as tetraalkylammonium, the planar acridine cations may improve the packing of the $[\text{Ni}(\text{dmit})_2]^-$ units. It has been showed previously that acridine cation can increase the dimensionality of a $[\text{Ni}(\text{dmit})_2]^-$ compound, leading to interesting conducting materials such as molecular metallic conductors [30,31]. Herein, we report the synthesis and characterization of three new $[\text{cation}][\text{Ni}(\text{dmit})_2]$ salts containing protonation acridinium, $[\text{AcrH}][\text{Ni}(\text{dmit})_2][\text{MeOH}]$ (**1**), $[\text{AcrH}]_2[\text{Ni}(\text{dmit})_2][\text{Cl}]$ (**2**) and $[\text{AcrH}]_2[\text{Ni}(\text{dmit})_2][\text{Br}]$ (**3**) (Scheme 1). Our results show that small changes in the chemical composition of these salts lead to significant difference in their crystal structure and physical properties. Compound **1** can self-assemble into high crystalline rod-shape crystals due to the abundant inter-molecular interactions. Compounds **2** and **3** represent the first examples where the halogen anions are incorporated into the separated sheets of $\text{Ni}(\text{dmit})_2$ units.

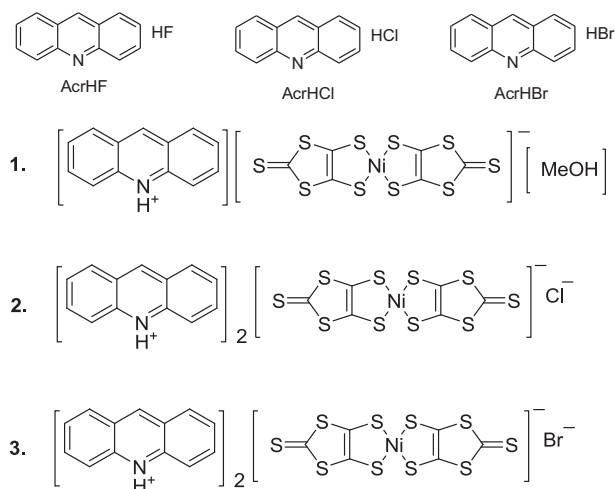
2. Experimental

2.1. Materials and physical measurements

$[\text{TBA}][\text{Ni}(\text{dmit})_2]$ (TBA = *n*-tetrabutylammonium) were prepared by the general method of Steimecke et al. [33], Steimecke and co-workers [34]. Acridine hydrochloride hydrate (AcrHCl)

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Scheme 1. The chemical structures of a series of protonation acridinium salts **AcrHF**, **AcrHCl**, **AcrHBr** and compounds **1–3**.

and acridine were purchased from commercial resources. All chemicals were reagent-grade and used as purchased without further purification.

Elemental analyses for C, H, N and S were determined using a Perkin–Elmer 240C analyzer. Infrared spectra were recorded in the 400–4000 cm^{-1} region by Vector22 Bruker spectrophotometer with KBr pellets. UV–Vis spectra were obtained on a UV–3100 spectrophotometer. Electrospray mass spectra (ESI-MS) were measured by a PE SCIEX API 365 LC/MS/MS system. Surface image of thin films were recorded by a LEO 1530 Scanning Electron Microscope (SEM). Selected area diffraction patterns were carried out using a transmission electron microscope (TEM) PHILIPS TEM 20. Magnetic susceptibility measurements of polycrystalline samples were measured over the temperature range 1.8–300 K with a Quantum Design MPMS-XL7 SQUID magnetometer and using an applied magnetic field of 2 kOe. Current–voltage (I–V) characteristics were performed by Keithley source meters connected with a probe station and measured under nitrogen atmosphere in a Mbraun glove box.

2.2. Synthesis of acridine hydrofluoride (AcrHF) and acridine hydrobromide (AcrHBr)

Acridine was dissolved in acetone, and excess HF (for AcrHF) or HBr (for AcrHBr) was added to this solution under stirring, and the solution was turned red immediately. After stirring for 30 min at room temperature, the solvent was removed under vacuum. A bright yellow precipitate was obtained. Those obtained products were used for the self-assembly reaction without further purifications.

2.3. Synthesis of [AcrH][Ni(dmit)₂][MeOH] (1)

A mixture of CH_3OH and CH_2Cl_2 (v/v, 1:1, 6 mL) was gently layered on top of a solution of the complex [TBA][Ni(dmit)₂] (6 mg, 0.01 mmol) in 2 mL of CH_2Cl_2 . A solution of AcrHF (3 mg, 0.01 mmol) in 2 mL of CH_3OH was added carefully as a third layer. The solution was left to stand for approximately 1 week at room temperature. Dark green needle crystals of **1** were obtained. Yield: 50%. ESI-MS: m/z (%): m/z 449.7 [Ni(dmit)₂]⁻. IR(KBr, cm^{-1}): 1633, 1587, 1464, 1340, 1252, 1064, 769. Elemental analysis (%) *Anal. Calc.* for $\text{C}_{20}\text{H}_{14}\text{NNiOS}_{10}$: C, 36.19; H, 2.12; N, 2.11. Found: C, 35.98; H, 2.19; N, 2.20%. UV–Vis (DMF), λ/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$):

326 (24 393), 340 (25 151), 386 (19 191), 445 (14 747), 588 (2878), 627 (3282), 1139 (17929).

2.4. Synthesis of [AcrH]₂[Ni(dmit)₂][Cl] (2)

A mixture of CH_3CN and CH_2Cl_2 (v/v, 1:1, 6 mL) was gently layered on top of a solution of the complex [TBA][Ni(dmit)₂] (6 mg, 0.01 mmol) in 2 mL of CH_2Cl_2 . A solution of AcrHCl (3 mg, 0.01 mmol) in 2 mL of CH_3CN was added carefully as a third layer. Dark green rhombus crystals of **2** were obtained after 3 days. Yield: 80%. ESI-MS: m/z (%): m/z 449.7 [Ni(dmit)₂]⁻. IR(KBr, cm^{-1}): 1639, 1352, 1286, 1252, 1058, 738. Elemental analysis (%) *Anal. Calc.* for $\text{C}_{32}\text{H}_{20}\text{ClN}_2\text{NiS}_{10}$: C, 45.36; H, 2.38; N, 3.31. Found: C, 45.16; H, 2.36; N, 3.29%. UV–Vis (DMF), λ/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 317 (25 505), 352 (32 222), 378 (21 414), 441 (14 192), 588 (2878), 627 (3282), 1140 (16 616).

2.5. Synthesis of [AcrH]₂[Ni(dmit)₂][Br] (3)

Compound **3** was synthesized by the same method using the AcrHBr as the starting material. Dark green block crystals of **3** were obtained after 1 week. Yield: 60%. ESI-MS: m/z (%): m/z 449.7 [Ni(dmit)₂]⁻. IR(KBr, cm^{-1}): 1637, 1350, 1280, 1056, 736. Elemental analysis (%) *Anal. Calc.* for $\text{C}_{32}\text{H}_{20}\text{BrN}_2\text{NiS}_{10}$: C, 43.10; H, 2.26; N, 3.14. Found: C, 43.26; H, 2.22; N, 3.18%. UV–Vis (DMF), λ/nm ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$): 320 (28 131), 355 (36 818), 378 (22 929), 440 (20 707), 445 (15 252), 588 (28 787), 627 (3282), 1139 (18 484).

2.6. X-ray structure determination

The crystal structures of compounds **1–3** were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were retrieved using SMART software and refined using SAINT [35] on all Observed reflections. Data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS [36] (supplied by Bruker). Structures were solved by direct methods using the program SHELXL-97 [37]. The positions of the metal atoms and their first coordination spheres were located from direct-method *E* maps; other non-hydrogen atoms were found using alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, were refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso} . Information for crystallographic data collection and structure refinement is summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The nickel compounds **1–3** were synthesized by a slow metathesis process by layering a CH_3CN or MeOH solution of AcrHF, AcrHCl and AcrHBr on the top of the CH_2Cl_2 solution of [TBA][Ni(dmit)₂]. The final solid products with different crystal shape were obtained: needle crystals for **1**, block crystal for **2** and **3**. They are all air stable in both the solid state and in solution at ambient temperature. All of the newly synthesized complexes were characterized by X-ray crystallography, elemental analyses, ESI-MS, UV–Vis and IR spectroscopy.

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