



# Studies on $\alpha$ - $C_3S_5^{2-}$ ( $dmit^{2-}$ ) and its dinuclear Ni(II) complex: spectroscopic and structural characterization

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## Abstract

The optical properties of the  $dmit^{2-}$  ion ( $dmit^{2-} = 4,5$ -dimercapto-1,3-dithiole-2-thiolate) have been characterized under a range of conditions. The oxidatively sensitive anion is highly solvatochromic:  $\lambda_{max} = 504$  (H<sub>2</sub>O), 514 (MeOH), 568 (MeCN), and 632 nm (DMF). With a shift in absorption maximum of  $4000\text{ cm}^{-1}$  (DMF versus H<sub>2</sub>O),  $dmit^{2-}$  is possibly the most solvatochromic species known. The dianion is monoprotonated by  $NH_4^+$  and binds  $CS_2$  to form a thioxanthate ( $C_3S_5 \cdot CS_2^{2-}$ ). <sup>13</sup>C NMR measurements of <sup>13</sup>C-enriched  $dmit^{2-}$  demonstrated that  $C_3S_5 \cdot CS_2^{2-}$  exchanges with free  $CS_2$  via an associative pathway involving binding of a second molecule of  $CS_2$ . Titration with acid showed that the  $M_2dmit$  ( $M = Na, Cs$ ) dissolves to give the dianion in protic solvents, rather than  $Hdmit^-$ . The conversion of  $\alpha$ - $C_3S_5^{2-}$  to its  $\beta$ -isomer ('Steimecke rearrangement') occurs very slowly with purified  $Na_2dmit$ , in contrast to the literature method. The salt  $(NBu_4)_2[Ni(dmit)_2]$  is also highly solvatochromic but its behavior does not follow any simple pattern. Treatment of  $(NBu_4)_2[Ni(dmit)_2]$  with 1/3 equiv. of  $[Ni(NCMe)_6](BF_4)_2$  gave the dinuclear compound  $(NBu_4)_2[Ni_2(dmit)_3]$ , the first Ni- $dmit^{2-}$  complex with a Ni/ $dmit^{2-}$  ratio that is not 1:2. The binuclear salt crystallizes as the  $CH_2Cl_2$  solvate as dark purple prisms. The planar  $Ni(dmit)_2^{2-}$  is bridged to  $Ni(dmit)$  via two sulfur atoms; the anion features a short Ni–Ni distance of 2.71 Å. ©2000 Elsevier Science Ltd All rights reserved.

**Keywords:** Dithiolene; Nickel; Dinuclear complexes; Acid–base; Solvatochromism; Carbon disulfide

## 1. Introduction

The inorganic heterocycle 4,5-dimercapto-1,3-dithiole-2-thione, with formula  $C_3S_5^{2-}$  referred to here as  $dmit^{2-}$ , is the basis for a substantial amount of research. The anion is of interest primarily as a precursor to electronic and photonic materials. This extensive research has been facilitated considerably by the efficient synthesis of  $dmit^{2-}$  by the alkali metal reduction of carbon disulfide [1–3]. In this preparation, a mixture of carbon disulfide and dimethylformamide is treated with sodium to give an equimolar mixture of the  $dmit^{2-}$  and trithiocarbonate ions. Separation of the two anions is readily achieved by treating the mixture with an aqueous solution of  $Zn^{2+}$ , which selectively complexes to the  $dmit^{2-}$  (Scheme 1).

The chemistry of  $dmit^{2-}$  can be roughly divided into three branches:

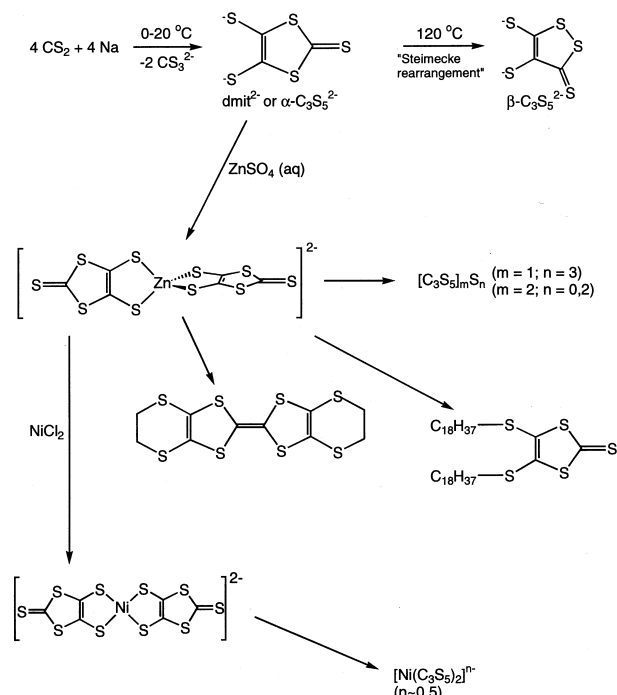
1. Organic derivatives, which are commonly related to the preparation of tetrathiafulvalenes [4], but have been extended to Langmuir–Blodgett films [5].

2. Binary carbon sulfides, illustrated by our recent synthesis of  $[C_8S_8]_n$  [6,7].

3. Coordination compounds, illustrated by  $[Ni(dmit)_2]^{2-}$  and organometallic derivatives, e.g.  $Cp_2Ti(dmit)$  [8–10].

The third area, coordination complexes of  $dmit^{2-}$ , especially those of nickel, has recently been particularly active. Since 1990, over 200 publications have appeared on derivatives of  $[Ni(dmit)_2]^{n-}$  ( $0 < n < 2$ ). This explosion of interest is attributable to the discovery that certain salts of  $[Ni(dmit)_2]^{n-}$  are metallic. A representative investigation in this area is the recent electrocrystallization of  $[Ni(dmit)_2]^{0.3-}$  with  $Li(15\text{-crown-5})^+$  as the counterion. The resulting material was found to be both an electrical and a lithium-ion conductor; such materials are sought for cathode materials in lithium-ion batteries [11]. In addition to displaying metallic conductivity, eight  $[M(dmit)_2]^{n-}$  salts ( $M = Ni, Pd$ ) are superconductors; they are the only transition-metal coordination compounds that have been found to display this property [12]. These remarkable electrical properties are attributed to the sulfur-rich exterior of these complexes that results in relatively strong intra- and inter-stack interactions. Recent work has shown that  $[Ni(dmit)_2]^{2-}$  exhibits a large third-order optical non linearity; hence appli-

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Scheme 1. Synthesis and reactions of  $[\text{Zn}(\text{dmit})_2]^{2-}$  and  $[\text{Ni}(\text{dmit})_2]^{2-}$ .

cations of these materials can be envisioned in the area of photonics [13].

While the organic and coordination chemistries of  $\text{dmit}^{2-}$  have been examined extensively [14], little attention has been paid to the properties of the dianion itself, as well as some fundamental aspects of its coordination chemistry. The UV–Vis spectrum of  $\text{dmit}^{2-}$  has been reported previously [15,16], but it appears that both of these reported spectra are not of actual  $\text{dmit}^{2-}$ , but rather the product of air oxidation. A separate report will describe the redox properties of  $\text{dmit}^{2-}$  and related thioanions [17].

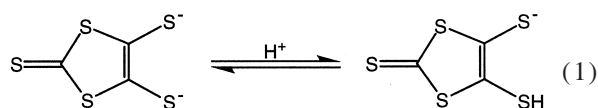
In this paper, the spectroscopic properties of  $\text{dmit}^{2-}$  are examined, and conclusions about the chemistry of this species are drawn from these properties. As indicated above, the  $[\text{Ni}(\text{dmit})_2]^{n-}$  system has been heavily examined for various oxidation states of nickel; this paper reports the first homoleptic Ni–dmit complex in which the dmit/ $\text{Ni}^{2+}$  ratio is other than 2:1 and illustrates a new bridging mode for the  $\text{dmit}^{2-}$  ligand [18–22].

## 2. Results and discussion

### 2.1. Acid–base properties of $\text{dmit}^{2-}$

One of the surprising properties of  $\text{dmit}^{2-}$  that has not been systematically investigated is its apparent solvatochromism (vide infra). Prior to investigating this property, we needed to determine whether the wide variety of absorption maxima exhibited by  $\text{dmit}^{2-}$  in various solvents is due to actual solvatochromism or to protonation of  $\text{dmit}^{2-}$  in protic solvents. DMF solutions of  $\text{Na}_2\text{dmit}$  and  $\text{Cs}_2\text{dmit}$  (the Cs salt

crystallizes well and is less hygroscopic than the sodium salt [23]) are deep blue, having a  $\lambda_{\text{max}}$  at 632 nm ( $\epsilon = 5510 \text{ M}^{-1} \text{ cm}^{-1}$ ). A DMF solution of  $\text{Cs}_2\text{dmit}$  turns red immediately on treatment with an excess of  $\text{NH}_4\text{Br}$ , with an absorption maximum (510 nm) close to that of a methanolic solution of  $\text{Na}_2\text{dmit}$  (514 nm), as shown in Fig. 1. We assign the red color in DMF to the monoprotonated species  $\text{dmitH}^-$  (Eq. 1), rather than the diprotonated species, because  $\text{H}_2\text{dmit}$ , which is deep yellow in solution, decomposes, eliminating  $\text{H}_2\text{S}$  to form  $\text{C}_6\text{S}_8$ , an insoluble solid [25].



Based on the similarity of the optical properties of  $\text{dmitH}^-$  in DMF and  $\text{dmit}^{2-}$  in methanol, we originally concluded that  $\text{dmit}^{2-}$  is so basic ( $\text{p}K_{\text{a}} > 15$ ) that it actually exists as  $\text{dmitH}^-$  in water and methanol. Subsequent investigations established, however, that  $\text{dmit}^{2-}$  indeed exists as a dianion in water and methanol [24]. A solution of  $\text{Cs}_2\text{dmit}$  in oxygen-free water ( $\lambda_{\text{max}} = 504 \text{ nm}$ ) has similar spectroscopic properties to those of a methanolic solution of  $\text{Na}_2\text{dmit}$ . No color change was observed after treatment with a large excess of  $\text{NaOH}$ ; this observation alone would mean that either  $\text{dmit}^{2-}$  exists as such in water, or that  $\text{dmit}^{2-}$  is extremely basic (i.e.  $\text{Hdmit}^-$  is not deprotonated by  $\text{NaOH}$ ).

To distinguish these possibilities, an aqueous  $\text{Cs}_2\text{dmit}$  solution was titrated (anaerobically) with  $\text{HCl}$ , monitoring by UV–Vis spectroscopy (Fig. 2). Isobestic behavior was observed at  $\leq 1$  equiv. of  $\text{HCl}$ ; the solution was yellow and homogeneous at that point. Only upon addition of  $> 1$  equiv. of  $\text{HCl}$  did a precipitate form; this precipitate is either  $\text{H}_2\text{C}_3\text{S}_5$  or its decomposition product  $\text{C}_6\text{S}_8$  [25]. Based on the data from the titration of  $\text{dmit}^{2-}$  with  $\text{HCl}$ , we conclude that  $\text{dmit}^{2-}$  exists as the dianion in both protic (water, methanol) and aprotic solvents (DMF). The conclusion that  $\text{dmit}^{2-}$  exists as the dianion in both protic and aprotic solvents means that the variation of color in different solvents is actually due

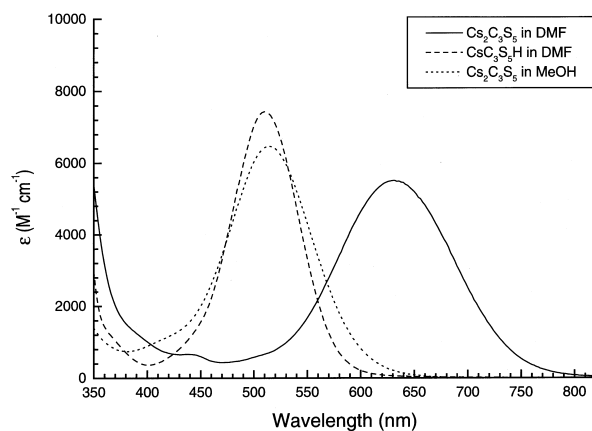


Fig. 1. Comparison of UV–Vis spectra of  $\text{Na}_2\text{dmit}$  in MeOH solution and  $\text{NaHdmit}$  in DMF solution, and UV–Vis spectrum of  $\text{Na}_2\text{dmit}$  in DMF solution.

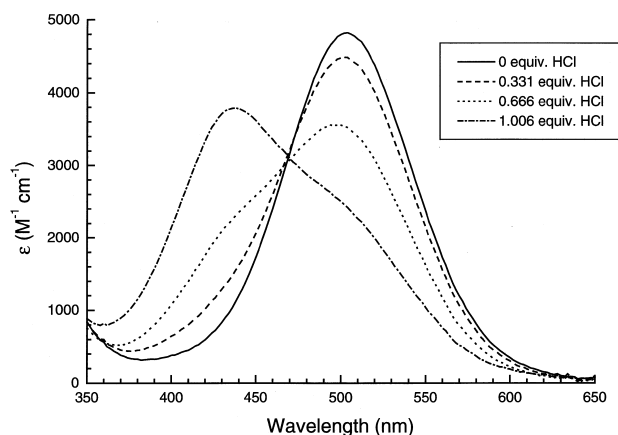


Fig. 2. UV-Vis spectra for the titration of aqueous  $\text{Cs}_2\text{dmit}$  with HCl.

to solvatochromism, and it is only coincidence that  $\text{dmitH}^-$  in DMF and  $\text{dmit}^{2-}$  in water/methanol have similar absorption maxima.

## 2.2. Optical properties of $\text{dmit}^{2-}$

The free anion,  $\text{dmit}^{2-}$ , can be made soluble in water and non-protic solvents, and is oxygen sensitive in all of them. The color of  $\text{dmit}^{2-}$  in solution is dependent on the solvent, ranging from red in water and methanol to blue in DMF. The most convenient preparation of the free anion involves the addition of excess NaOMe to a methanolic suspension of the thioester,  $\text{C}_3\text{S}_5[\text{C}(\text{O})\text{Ph}]_2$  [26], giving  $\text{Na}_2\text{dmit}$  as a red solution (Eq. 2) ( $\lambda_{\text{max}} = 514 \text{ nm}$ ,  $\epsilon = 5710 \text{ M}^{-1} \text{ cm}^{-1}$ ), having an absorption maximum at 514 nm.

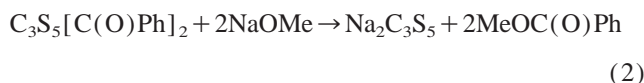


Fig. 3 shows the UV-Vis spectrum of  $\text{Na}_2\text{dmit}$  in methanol before and after exposure to air for a few seconds. The yellow coloration for  $\text{dmit}^{2-}$  solutions ( $\lambda_{\text{max}} = 438 \text{ nm}$ ) indicates oxidation. The red color of authentic  $\text{Na}_2\text{dmit}$  in methanol ( $\lambda_{\text{max}} = 514 \text{ nm}$ ) has been described by Svenstrup, Matsubayashi and others [4,27], and these results were confirmed by us. The absorption maximum of  $\text{Na}_2\text{dmit}$  in ethanol has however been listed by Reuter and Gattow to be 412 nm [15], which may actually be this yellow oxidized species. Removing the solvent from a methanolic  $\text{Na}_2\text{dmit}$  solution and adding dry, oxygen-free acetonitrile results in a purple solution ( $\lambda_{\text{max}} = 568 \text{ nm}$ ). As shown in Fig. 4, this solution also turns yellow within seconds on exposure to air ( $\lambda_{\text{max}} = 472 \text{ nm}$ ). Singh and Singh [16] recently listed the absorption of  $\text{Na}_2\text{dmit}$  in acetonitrile to be 475 nm; again, based on the similarities of the listed absorption maxima, the compound they examined appears to have been an oxidized derivative of  $\text{dmit}^{2-}$ .

Because the energy of the absorption maximum increases with increasing solvent polarity, the effect is characterized as hypsochromism. The difference between the absorption maxima for  $\text{dmit}^{2-}$  in water and in DMF corresponds to 4020

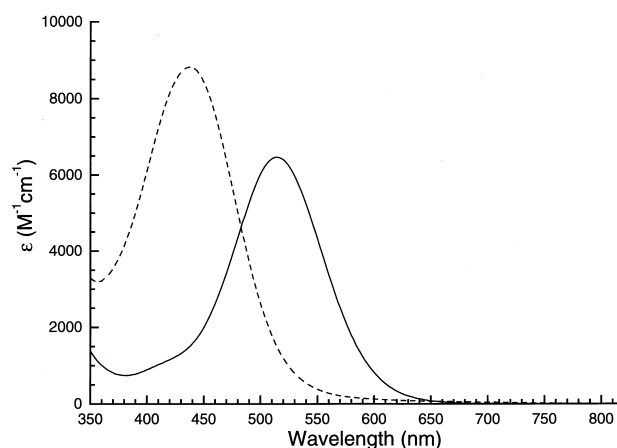


Fig. 3. UV-Vis spectra of  $\text{Na}_2\text{dmit}$  in MeOH solution before (solid) and after (dotted) oxidation with air.

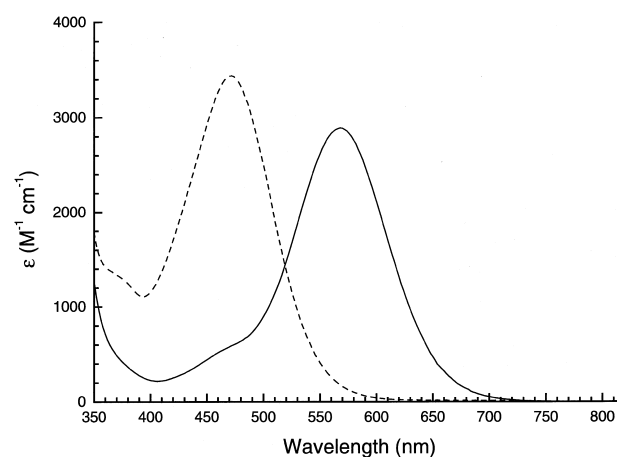


Fig. 4. UV-Vis spectra of  $\text{Na}_2\text{dmit}$  in MeCN solution before (solid) and after (dotted) oxidation with air.

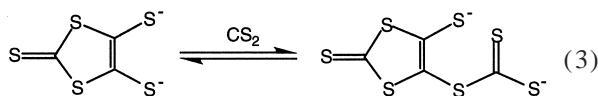
$\text{cm}^{-1}$ ; this response to solvent polarity is comparable to (or exceeds) the most solvatochromic compounds known. One such compound is a merocyanine dye [28] with a difference in absorbance maxima of  $9500 \text{ cm}^{-1}$ , but this is between toluene and water, which is a greater range of polarity than is available for  $\text{dmit}^{2-}$  due to solubility constraints.

## 2.3. The $\text{dmit}^{2-}$ - $\text{CS}_2$ system

In the most widely used synthetic route to  $\text{dmit}^{2-}$ ,  $\text{CS}_2$  is reduced with sodium metal in DMF solution. The  $\text{dmit}^{2-}$  anion is not isolated directly; instead, it is usually coordinated to  $\text{Zn}^{2+}$  and isolated as the salt,  $(\text{R}_4\text{N})_2[\text{Zn}(\text{C}_3\text{S}_5)_2]$ . Prior to the addition of zinc, however, the  $\text{dmit}^{2-}$  solution is bright red. Such a solution should be anhydrous and highly basic, considering the presence of the  $\text{Na}_2\text{CS}_3$  byproduct and the excess Na. It is therefore inconceivable that such a solution would contain a significant amount of the protonated species,  $\text{dmitH}^-$ . Another explanation is required to explain the red color of the reaction mixture, rather than the blue color ( $\lambda_{\text{max}} = 632 \text{ nm}$ ) observed for  $\text{M}_2\text{dmit}$  in DMF ( $\text{M} = \text{Na}, \text{Cs}$ ).

We initiated a series of experiments based on the hypothesis that the red coloration of the crude (but anhydrous) reaction solutions is due to adducts of  $\text{CS}_2$  and  $\text{dmit}^{2-}$ .  $\text{CS}_2$  is known to form adducts with a variety of nucleophiles, including thiolates [29–31], and  $\text{CS}_2$  is usually used in a large excess in the synthesis of  $\text{dmit}^{2-}$ . Furthermore, the  $\text{CS}_2$  adduct of  $\beta\text{-C}_3\text{S}_5^{2-}$  (an isomer of  $\text{dmit}^{2-}$ , see Scheme 1) has been crystallographically characterized [32]. We found that the addition of  $\text{CS}_2$  to a DMF solution of  $\text{Cs}_2\text{dmit}$  effected an immediate color change from blue to the red color of the synthesis solution ( $\lambda_{\text{max}} = 490 \text{ nm}$ ).

We further investigated the nature of the  $\text{CS}_2$ – $\text{dmit}^{2-}$  reaction through  $^{13}\text{C}$  NMR studies using  $^{13}\text{C}$ -enriched  $\text{dmit}^{2-}$ . Due to the high cost of  $^{13}\text{CS}_2$ , we first modified the synthesis of  $\text{dmit}^{2-}$  so that it uses  $\text{CS}_2$  more efficiently. Fig. 5 shows a  $^{13}\text{C}$  NMR spectrum of a DMF- $d_7$  solution of  $^{13}\text{C}$ -enriched  $\text{dmit}^{2-}$ .  $^{13}\text{C}$  NMR resonances are observed at  $\delta$  209 and 144, which are assigned to the thiocarbonyl and the alkenyl centers, respectively. Upon treatment of this solution with an excess of unlabeled  $\text{CS}_2$  ( $\delta$  193), a new species was formed, having signals at  $\delta$  214 (C=S) and broad signals at  $\delta$  172 and 122. The latter two peaks are assigned to the now-inequivalent alkenyl carbon centers of the  $\text{CS}_2$  monoadduct of  $\text{dmit}^{2-}$  (Eq. 3).



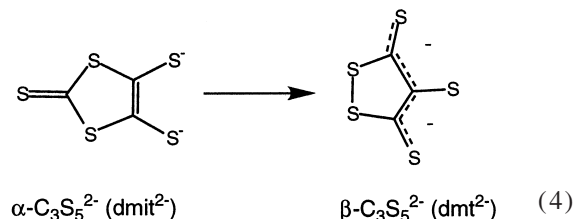
The broadness of these alkenyl peaks is attributed to an exchange of the trithiocarbonate and thiolate functions.

The excess  $\text{CS}_2$  was then removed from the DMF solution by distillation under reduced pressure. The  $^{13}\text{C}$  NMR spectrum of the resulting purplish solution shows the absence of

free  $\text{CS}_2$  and resonances corresponding to both  $\text{dmit}^{2-}$  and  $\text{C}_3\text{S}_5 \cdot \text{CS}_2^{2-}$ .

#### 2.4. Comments on the Steimecke rearrangement

It is well known that a mixture of sodium and carbon disulfide in DMF, when heated to  $120^\circ\text{C}$ , produces an isomer of  $\text{dmit}^{2-}$ , which we previously termed [25]  $\beta\text{-C}_3\text{S}_5^{2-}$  (Eq. 4).



It was of interest to know whether this isomerization mechanism is intramolecular or whether other species are involved. UV–Vis spectroscopy would be suitable for monitoring this isomerization because of the different optical properties of the two isomers: the  $\lambda_{\text{max}}$  of  $\text{dmit}^{2-}$  in DMF is 632 nm (blue color, as stated above), while the  $\lambda_{\text{max}}$  of  $\beta\text{-C}_3\text{S}_5^{2-}$  in DMF is 530 nm (red color). A DMF solution of  $\text{Na}_2\text{dmit}$  remained unchanged after 24 h at  $120^\circ\text{C}$ , based on UV–Vis measurements. This initial experiment was conducted at a concentration ( $6 \times 10^{-5} \text{ M}$ ) appropriate for UV–Vis spectroscopy. Recognizing the possibility that the rearrangement might be bimolecular, the experiment was repeated at a concentration (0.8 M) closer to that typically used in a reaction mixture [25]; however, the characteristic color change required approximately 15 days at  $120^\circ\text{C}$ . Evidently a catalyst, which we have not identified, is present in the reaction mixture when the Steimecke rearrangement is carried out.

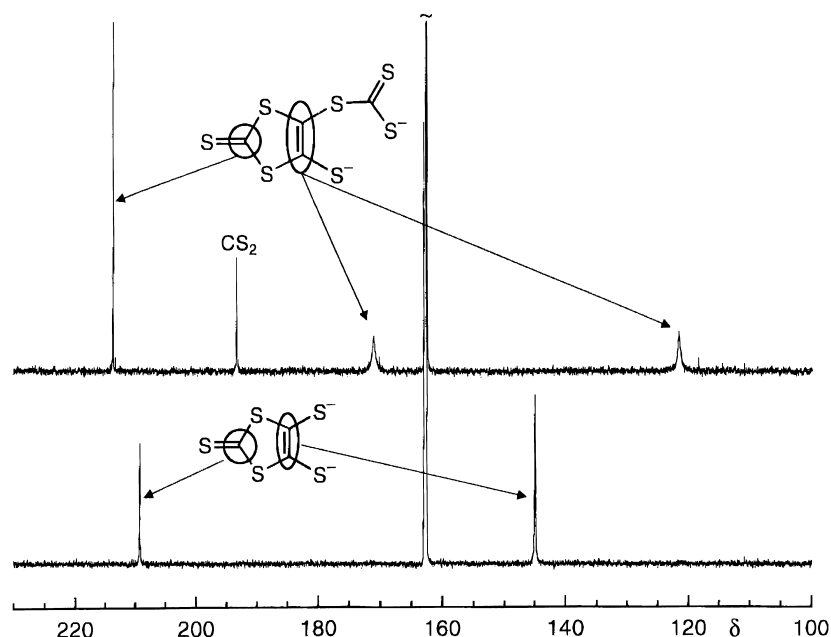


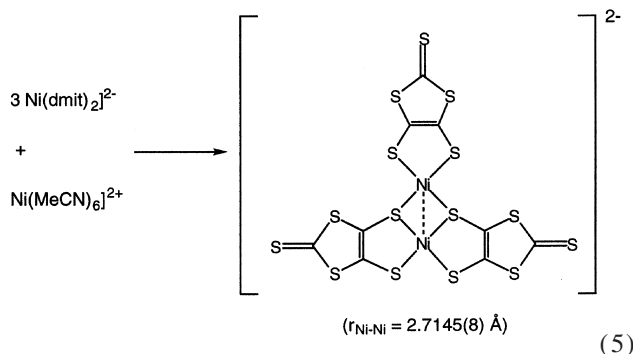
Fig. 5. 125 MHz  $^{13}\text{C}$  NMR spectra (DMF- $d_7$ ) of  $\text{Cs}_2\text{dmit}$  (bottom),  $\text{Cs}_2\text{dmit}$  with excess  $\text{CS}_2$  added (middle), and with most of the  $\text{CS}_2$  removed (top).

## 2.5. Comments on the optical properties of $[\text{Ni}(\text{dmit})_2]^{2-}$

We began this aspect of the work by examining the solution properties of  $[\text{Ni}(\text{dmit})_2]^{2-}$ , the precursor to many conductive materials [33,34]. Spectrophotometric measurements show that  $(\text{NBu}_4)_2[\text{Ni}(\text{dmit})_2]$  is highly solvatochromic. The position of its absorption maximum does not, however, correlate with the  $E_T(30)$  or the  $E_T^N$  solvent index of Reichardt and Harbusch-Goernert [35] of the solvent. THF ( $E_T^N=0.207$ ) solutions are blue, with a  $\lambda_{\text{max}}$  of 596 nm. DMF ( $E_T^N=0.386$ ) solutions are green, with a  $\lambda_{\text{max}}$  of 626 nm. This would seem to indicate that the compound is bathochromic; however, the trend reverses for acetonitrile ( $E_T^N$  index = 0.46,  $\lambda_{\text{max}}=596$  nm, blue solution) and methanol ( $E_T^N$  index = 0.762,  $\lambda_{\text{max}}=554$  nm, purple solution). There may be other factors affecting the absorption maximum besides solvatochromism, such as dimerization or ligation of a solvent.

## 2.6. Synthesis and structure of $[\text{Ni}_2(\text{dmit})_3]^{2-}$

While the  $[\text{Ni}(\text{dmit})_x]^{n-}$  system has been investigated for many values of  $n$ , variations in  $x$ , the Ni/dmit ratio, have not been reported. Treatment of an acetonitrile solution of  $(\text{NBu}_4)_2[\text{Ni}(\text{dmit})_2]$  with 1/3 equiv. of  $[\text{Ni}(\text{MeCN})_6]^{2+}$  gave a red solution containing the salt  $(\text{NBu}_4)_2[\text{Ni}_2(\text{dmit})_3]$  (Eq. 5).



In contrast to  $[\text{Ni}(\text{dmit})_2]^{2-}$ , solutions of the dinickel compound are sensitive to oxygen. This finding is somewhat counterintuitive because the negative charge is delocalized over a larger molecule. A major product of air oxidation of this compound was characterized crystallographically to be  $(\text{NBu}_4)_2[\text{Ni}(\text{dmit})_2]$ , which is well known [36–38].

The structure of  $(\text{NBu}_4)_2[\text{Ni}_2(\text{dmit})_3]$  was established by single crystal X-ray diffraction (Fig. 6). The anion is binuclear with two bridging dmit ligands such that the complex has idealized  $C_s$  symmetry. Bond lengths and angles are listed in Table 1. The noteworthy feature is the Ni–Ni distance of 2.7145(8) Å. An example of a compound with an unsupported Ni–Ni bond is  $[\text{Ni}(\text{C}_{10}\text{H}_{14}\text{N}_8)]_2$  [39], with a Ni–Ni bond distance of 2.788(2) Å. This establishes that the nickel–nickel distance observed in this work is close enough to be characterized as a bond. The ethanedithiolate derivative  $[\text{Ni}_2(\text{S}_2\text{C}_2\text{H}_4)_3]^{2-}$  [40] has a wider average Ni–S–Ni angle

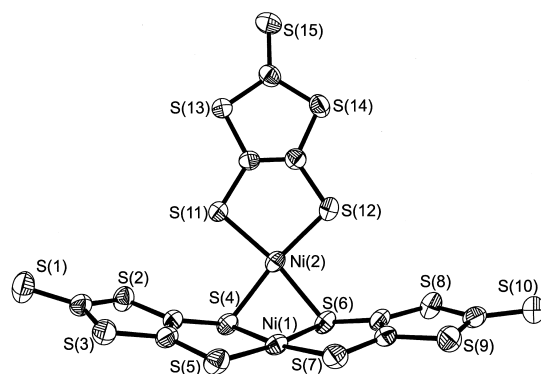


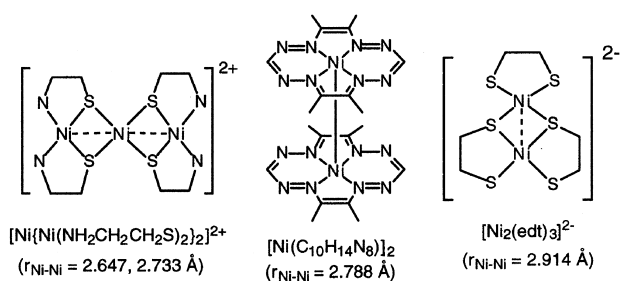
Fig. 6. The molecular structure of the anion,  $[\text{Ni}_2(\text{dmit})_3]^{2-}$ , with thermal ellipsoids at the 50% probability level.

Table 1

Selected bond lengths (Å) and angles (°) for the anion in  $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_3\text{S}_5)_3] \cdot \text{CH}_2\text{Cl}_2$

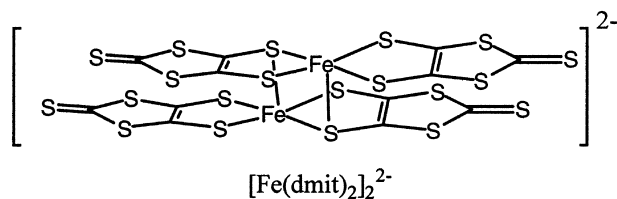
Ni(1)–Ni(2)	2.7145(8)	S(4)–C(4)	1.745(5)
Ni(1)–S(7)	2.1699(13)	S(11)–C(1)	1.734(5)
Ni(1)–S(4)	2.1696(13)	S(12)–C(2)	1.745(5)
Ni(1)–S(6)	2.1803(14)	C(4)–C(5)	1.349(6)
Ni(1)–S(5)	2.1839(14)	C(2)–C(1)	1.354(6)
Ni(2)–S(12)	2.1699(14)	C(7)–C(8)	1.353(6)
Ni(2)–S(11)	2.1794(13)		
Ni(2)–S(4)	2.2367(14)	Ni(1)–S(4)–Ni(2)	76.04(4)
Ni(2)–S(6)	2.2449(13)	Ni(1)–S(6)–Ni(2)	75.66(4)
S(6)–C(7)	1.747(5)	S(7)–Ni(1)–S(4)	171.96(6)
S(5)–C(5)	1.735(5)	S(6)–Ni(1)–S(5)	173.40(5)
S(7)–C(8)	1.730(5)	S(4)–Ni(1)–S(5)	94.29(5)
		S(4)–Ni(2)–S(6)	77.63(5)

(83.4°) than that observed here (75.8°) and a correspondingly longer Ni–Ni distance (2.914(1) Å).



Although not completely analogous in structure, an example of a short Ni–Ni bond distance bridged by a thiolate is the cation  $[\text{Ni}\{\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2\}_2]^{2+}$  [41]. Here, the two nickel–nickel distances are 2.733 and 2.647 Å, the range of these distances indicates the ‘softness’ of the Ni–Ni interaction. An explanation is required for an apparently attractive interaction involving a pair of filled  $3d_z^2$  orbitals. Under lower symmetry, the  $3d_z^2$  orbitals mix with empty  $4p_z$  orbitals. This mixing lowers the energies of the  $3d_z^2$  orbitals, resulting in a weak bonding interaction overall. The idealized symmetry environment around the nickel atoms in  $[\text{Ni}_2(\text{dmit})_3]^{2-}$  is  $C_s$ , which would also allow for mixing of the  $3d_z^2$  and  $4p_z$  orbitals on the nickel centers.

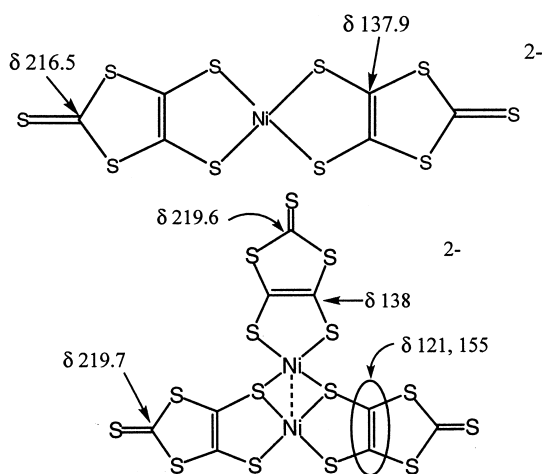
Although no compound has been structurally characterized in which  $\text{dmit}^{2-}$  bridges two metal centers in an analogous fashion to  $[\text{Ni}_2(\text{dmit})_3]^{2-}$ , there are other examples of bridging  $\text{dmit}^{2-}$  ligands, such as in the  $\text{Cp}_2^*\text{Fe}^+$  salt of  $[\text{Fe}(\text{dmit})_2]_2^{2-}$  [20].



In this anionic dimer, the iron atoms are in a square pyramidal environment. Only one thiolate sulfur from the  $\text{dmit}^{2-}$  ligand functions as a bridging ligand. The Fe–S bond lengths, both within and between  $[\text{Fe}(\text{dmit})_2]^-$  units, are all  $2.24 \pm 0.01 \text{ \AA}$ .

$^{13}\text{C}$  NMR measurements were conducted on solutions of  $[\text{Ni}_2(\text{dmit})_3]^{2-}$  in order to establish its solution structure. Due to the lack of nOe effects and limited solubility, these measurements were carried out using a 10 mm sample tube and  $\text{dmit}^{2-}$  that was  $\sim 16\%$   $^{13}\text{C}$ . The  $^{13}\text{C}$  NMR spectrum of  $(\text{NBu}_4)_2[\text{Ni}(\text{dmit})_2]$  features resonances at 216.5 and 137.9 [42].

On the basis of the crystallographic results, one would expect five resonances for  $[\text{Ni}_2(\text{dmit})_3]^{2-}$ : three for the ethylenic carbon atoms and two for the thiocarbon atoms. The  $^{13}\text{C}$  NMR spectrum is shown in Fig. 7. Due to the  $^{13}\text{C}$  enrichment,  $^{13}\text{C}$ – $^{13}\text{C}$  coupling is evident as satellites around two of the peaks. The assignments for the peaks are as follows:



The peaks at  $\delta 121$  and  $155$  can be assigned to the alkenyl carbons in the  $\text{Ni}(\text{dmit})_2$  moiety because the satellites indicate coupling to a carbon in a different environment. The peak at  $\delta 138$  has no satellites, so it can be assigned to the other alkenyl carbons. The thione carbons are in such similar environments that their chemical shifts differ by only 0.1 ppm.

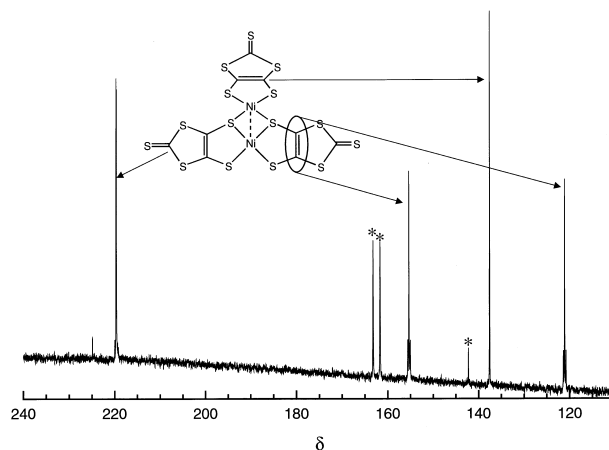
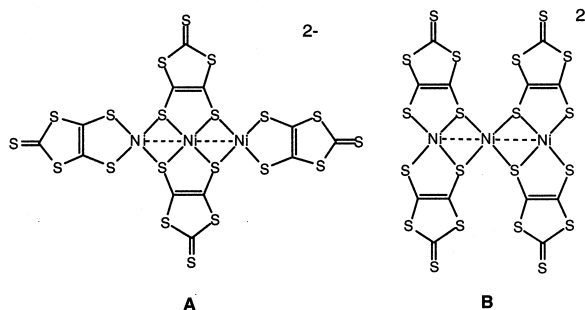


Fig. 7. 125 MHz  $^{13}\text{C}$  NMR spectra ( $\text{CD}_2\text{Cl}_2$ ) of  $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{dmit})_3]$ . The peaks labeled with asterisks are assigned to a higher nuclearity impurity discussed in Section 2.7.

### 2.7. Higher oligomers of $\text{Ni}$ – $\text{dmit}^{2-}$

Inspection of the  $^{13}\text{C}$  NMR spectrum of  $[\text{Ni}_2(\text{dmit})_3]^{2-}$  reveals two additional peaks at  $\delta 162$  and  $163$ . We attribute these to the alkenyl carbon atoms in a higher-nuclearity derivative of  $\text{Ni}(\text{dmit})_2^{2-}$ . Two possible structures of this impurity are shown below.



Both of these structures would have two types of ethylenic carbons. The ethanedithiolate analog of **B** is known [43]. However, **A** appears to be the more plausible in this case due to the lack of  $^{13}\text{C}$ – $^{13}\text{C}$  coupling in its NMR spectrum. The  $^{13}\text{C}$  NMR spectrum of  $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{dmit})_3]$  in acetone- $d_6$  shows no evidence for this higher-nuclearity impurity.

Combining MeCN solutions of  $\text{Ni}(\text{dmit})_2^{2-}$  and  $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$  in a 1:1 ratio produced a greenish solid, which analyzed as  $(\text{Bu}_4\text{N})_2[\text{Ni}_{15}(\text{dmit})_{16}]$ . A similar study was carried out on the nickel complex of the  $\beta\text{-C}_3\text{S}_5^{2-}$ . Treatment of  $(\text{Bu}_4\text{N})_2[\text{Ni}(\beta\text{-C}_3\text{S}_5)_2]$  with  $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$  resulted only in an insoluble product; no intermediate products were detected. The black solid analyzed as  $\text{NiC}_3\text{S}_5$ , and preliminary electrical measurements on a pressed pellet of this solid showed it to be insulating.

### 3. Summary

The following are the principal conclusions of this study.

1. The  $\text{dmit}^{2-}$  ion is strongly solvatochromic, having an absorption that shifts to higher energy with increasing

solvent polarity. Its color in solution ranges from red in water and methanol to blue in DMF.

2. Aqueous and alcoholic solutions of  $\text{dmit}^{2-}$  indeed consist of the dianion, not the monoprotonated monoanion,  $\text{Hdmit}^-$ . The extreme solvatochromism combined with the oxygen sensitivity has been the source of previous confusion in this area.
3.  $\text{CS}_2$  reversibly binds  $\text{dmit}^{2-}$  to give the thioxanthate ( $\text{C}_3\text{S}_5 \cdot \text{CS}_2^{2-}$ ). This adduct exchanges with free  $\text{CS}_2$ .
4. DMF solutions of pure  $\text{dmit}^{2-}$  undergo the Steimecke rearrangement much more slowly than in the reaction mixture used for  $\beta\text{-C}_3\text{S}_5^{2-}$  synthesis.
5. The well known anion  $[\text{Ni}(\text{dmit})_2]^{2-}$  reacts with a source of  $\text{Ni}^{2+}$  to form  $[\text{Ni}_2(\text{dmit})_3]^{2-}$ , which features a short Ni–Ni distance ( $\sim 2.71 \text{ \AA}$ ).

## 4. Experimental

### 4.1. Materials and methods

$^{13}\text{CS}_2$  was obtained from Cambridge Isotopes (Cambridge, OH, USA).  $[\text{Ni}(\text{MeCN})_6](\text{BF}_4)_2$  was prepared from Ni metal and  $\text{NOBF}_4$  [44]. The  $\text{C}_3\text{S}_5(\text{COPh})_2$  was prepared from the treatment of  $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{C}_3\text{S}_5)_2]$  [2] with benzoyl chloride [1]. Unless otherwise noted, reactions and work-ups were conducted under nitrogen using degassed solvents. Electronic spectra were collected using an HP8452 diode-array spectrophotometer. A 1 cm path length cell was used.

### 4.2. Synthesis

#### 4.2.1. Preparation of $^{13}\text{C}$ -enriched $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{C}_3\text{S}_5)_2]$

The usual methods for the preparation of  $\text{dmit}^{2-}$  [2,45] were revised so as to make the most efficient use of  $^{13}\text{CS}_2$ , which is expensive. The  $^{13}\text{CS}_2$  was diluted with five portions of isotopically normal  $\text{CS}_2$ . An alloy was prepared from potassium metal (0.94 g, 0.0233 mol) and sodium metal (0.515 g, 0.0224 mol), and was chilled to  $0^\circ\text{C}$ . Distilled DMF (10 ml) was added, followed by  $^{13}\text{C}$ -enriched  $\text{CS}_2$ , prepared as above (2.41 ml, 0.0401 mol). The mixture took on a yellow color immediately, which progressed through orange to a deep red within 15 min. The reaction mixture was allowed to warm to room temperature over the course of 24 h, after which the mixture became a purplish-blue, porous semisolid. Residual alkali metal was oxidized with isopropanol (20 ml), followed by a few milliliters of ethanol. After 0.5 h, most of the alcohols were removed by evaporation. The purple DMF solution was treated with a solution of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (1.44 g, 5.01 mmol) in water (50 ml), chilled to  $0^\circ\text{C}$ , and treated with a solution of  $\text{Bu}_4\text{NBr}$  (3.24 g, 10.1 mmol) in water (50 ml). A fine red powder formed, which was collected. This was recrystallized by dissolution in  $\sim 20$  ml of acetone, diluting with a similar volume of methanol, and successively concentrating and diluting with methanol until red crystals

formed, which were washed with ether. Yield: 2.32 g, 49% based on  $\text{CS}_2$ .

#### 4.2.2. Preparation and characterization of $\text{dmit}^{2-}$

$\text{Cs}_2\text{C}_3\text{S}_5 \cdot 1.5\text{H}_2\text{O}$  was prepared from  $\text{C}_3\text{S}_5(\text{COPh})_2$  and  $\text{CsOH} \cdot \text{H}_2\text{O}$  according to the method of Gasiorowski et al. [24]. The  $^{13}\text{C}$  NMR spectrum was collected of a solution of the  $^{13}\text{C}$ -enriched  $\text{Cs}_2\text{C}_3\text{S}_5$  (0.06 g, 0.12 mmol in  $\sim 0.8$  ml of  $\text{DMF-}d_7$ ). UV–Vis spectroscopic characterization was carried out by charging a sealed cuvette with a DMF solution (10 ml, 0.12 mM) of  $\text{Cs}_2\text{C}_3\text{S}_5 \cdot 1.5\text{H}_2\text{O}$  in an inert atmosphere chamber.  $^{13}\text{C}$  NMR ( $\text{DMF-}d_7$ ):  $\delta$  209, 145. UV–Vis,  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 628 (5500). The solution used for the UV–Vis measurement (4 ml,  $1.2 \times 10^{-4}$  M) was treated with 0.02 g (0.2 mmol) of  $\text{NH}_4\text{Br}$ , which did not fully dissolve. UV–Vis,  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 510 (7430).

#### 4.2.3. $^{13}\text{C}$ NMR monitoring of the $\text{dmit}^{2-} + \text{CS}_2$ reaction

The solution of 0.06 g (0.12 mmol) of  $^{13}\text{C}$ -enriched  $\text{Cs}_2\text{dmit}$  used for the  $^{13}\text{C}$  NMR spectroscopic characterization (see above) was treated with 0.08 ml of isotopically normal  $\text{CS}_2$  (1.3 mmol), causing the color to turn from blue to orange–red immediately.  $^{13}\text{C}$  NMR ( $\text{DMF-}d_7$ ):  $\delta$  213, 193 ( $\text{CS}_2$ ), 171 (br), 122 (br). Most of the  $\text{CS}_2$  was then removed by subjecting the red solution briefly to a dynamic vacuum, causing the color to turn from orange–red to purple.  $^{13}\text{C}$  NMR ( $\text{DMF-}d_7$ ):  $\delta$  213, 171, 122. See Fig. 5.

#### 4.2.4. $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_3\text{S}_5)_3] \cdot \text{CH}_2\text{Cl}_2$

The  $^{13}\text{C}$ -labeled nickel coordination compound,  $(\text{Bu}_4\text{N})_2[\text{Ni}(*\text{C}_3\text{S}_5)_2]$  ( $*\text{C} = 16\% \text{ }^{13}\text{C}$ ), was prepared from  $(\text{Bu}_4\text{N})_2[\text{Zn}(*\text{C}_3\text{S}_5)_2]$  according to literature procedures [1]. A solution of 0.1790 g (0.1910 mmol) of  $(\text{Bu}_4\text{N})_2[\text{Ni}(*\text{C}_3\text{S}_5)_2]$  in acetonitrile (20 ml) was treated with a solution of  $[\text{Ni}(\text{NCCH}_3)_6](\text{BF}_4)_2$  (0.0321 g, 0.064 mmol) in  $\text{CH}_3\text{CN}$  (0.5 ml). Within seconds, the color of the solution changed from green to red. The MeCN was removed by evaporation, and the residue extracted into  $\text{CH}_2\text{Cl}_2$  in  $\sim 0.5$  ml. Dilution with diethyl ether ( $\sim 1$  ml) produced dark purple crystals. Yield: 0.1454 g, 96%. Anal. Calc. for  $\text{C}_{42}\text{H}_{74}\text{N}_2\text{Cl}_2\text{Ni}_2\text{S}_{15}$ : C, 39.52; H, 5.84; N, 2.19. Found: C, 39.54; H, 6.03; N, 2.07%.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  121 (s, 16% d,  $J_{\text{C-C}} = 0.6$  Hz), 138 (s), 155 (s, 16% d,  $J_{\text{C-C}} = 0.6$  Hz), 162 (s), 163 (s), 219.6 (s), 219.7 (s).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  121 (s, 16% d,  $J_{\text{C-C}} = 0.6$  Hz), 138 (s), 156 (s, 16% d,  $J_{\text{C-C}} = 0.6$  Hz), 220 (s).

#### 4.2.5. Titration of $\text{Cs}_2\text{C}_3\text{S}_5$ with HCl

$\text{Cs}_2\text{C}_3\text{S}_5$  (32.0 mg, 69.2  $\mu\text{mol}$ ) was dissolved in deionized, oxygen-free water (12.46 ml) to make a 5.56 mM ‘stock’ solution. This solution was treated with 1 equiv. of HCl in steps of 0.1 equiv. After each step, a UV–Vis spectrum was collected by diluting a small aliquot of the reaction mixture to about 0.06 mM in a 1 cm path length cuvette fitted with a valve to exclude air. In calculating the equivalents added, the

total amount of  $\text{Cs}_2\text{C}_3\text{S}_5$  was adjusted for the aliquots used for the measurements.

#### 4.2.6. Attempted Steimecke rearrangement of $\text{Na}_2\text{dmit}$

Sodium metal (0.0247 g, 1.07 mmol) was allowed to react with 8 ml of MeOH. To this solution was added the thioester  $\text{C}_3\text{S}_5(\text{COPh})_2$ . This yellow slurry was allowed to react for 30 min at ambient temperature, then the methanol was removed by evaporation. The pink residue was washed with ether ( $4 \times 15$  ml) to remove the methyl benzoate byproduct. Anhydrous DMF (7.5 ml) was added to the residue, resulting in a blue solution of the  $\text{dmit}^{2-}$  salt and solid NaOH. An aliquot (15 ml) of the solution was decanted from the NaOH and added to DMF (7.5 ml) in a 1 cm path length cell (conc.  $5.9 \times 10^{-5}$  M). No change, either in appearance or UV–Vis spectroscopic properties, was observed after 3.8 h at  $100.5^\circ\text{C}$ . 0.8 M solution of  $\text{Na}_2^- \text{dmit}$  ( $\sim 1$  ml), prepared in a similar manner, was then flame-sealed in a Pyrex tube and maintained at  $12^\circ\text{C}$ . No color change was observed after 21 h. After 15 days, the color was deep brown.

#### 4.2.7. Crystallographic analysis of $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_3\text{S}_5)_3] \cdot \text{CH}_2\text{Cl}_2$

A  $\text{CH}_2\text{Cl}_2$  solution of  $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_3\text{S}_5)_3] \cdot \text{CH}_2\text{Cl}_2$  was layered with diethyl ether. A black, prismatic crystal of approximate dimensions  $0.14 \times 0.14 \times 0.18$  mm was selected for analysis and mounted on a glass fiber with Paratone-E (Exxon). Intensity data were collected at 198(2) K using a Siemens CCD area detector utilizing Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The completeness of data collection in the range  $2\theta = 3.22$  to  $56.56^\circ$  was 96.5%. The data were corrected for absorption using the empirical method with maximum and minimum transmission factors of 0.9901 and 0.8546, respectively. The data merged to form a set of 14320 independent reflections with  $R_{\text{int}} = 0.0734$ . The space group,  $P2_1/n$  (no. 14), was selected on the basis of systematic conditions and was verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ . Hydrogen atom positions were calculated using a riding model. All non-hydrogen atoms were refined anisotropically. The SOF for one of the butyl groups was refined between two positions. The largest peak and hole in the difference map was  $0.529$  and  $-0.509 \text{ e \AA}^{-3}$ , respectively. Additional crystal data:  $a = 17.7947(5)$ ,  $b = 14.4605(4)$ ,  $c = 23.7863(6) \text{ \AA}$ ;  $\beta = 102.38^\circ$ ;  $V = 5978.9(3) \text{ \AA}^3$ ;  $Z = 4$ ;  $\rho(\text{calc}) = 1.418 \text{ Mg m}^{-3}$ ;  $\mu = 1.274 \text{ mm}^{-1}$ ; index ranges  $-18 \leq h \leq 23$ ,  $-19 \leq k \leq 19$ ,  $-31 \leq l \leq 14$ ; number of data and parameters 14320 and 595, respectively; final  $R_1/wR_2$  ( $I > 2\sigma(I)$ ) 0.0665/0.1032; GoF = 1.077.

#### Supplementary data

Supplementary data are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@

ccdc.cam.ac.uk) on request, quoting the deposition number CCDC 133733.

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