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Tetrathieno[2,3-b]porphyrazines: Thiophene Analogues of Phthalocyanines: A Re-investigation

Robert M. Christie & Brian G. Freer

Department of Textiles, The Scottish College of Textiles, Netherdale, Galashiels TD1 3HF, Scotland, UK

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ABSTRACT

The chemistry leading to the formation of tetrathieno[2,3-b]porphyrazines, which may be considered as thiophene analogues of phthalocyanines, previously reported in Linstead's early work on the phthalocyanines and related compounds, has been re-examined and some of the synthetic difficulties explored. The electronic spectral data for four metal complexes of the parent system and the correlation of the data with the results of PPP MO calculations are reported. © 1997 Published by Elsevier Science Ltd. All rights reserved

Keywords: phthalocyamines; thiophene; PPP MO calculations; electronic spectra.

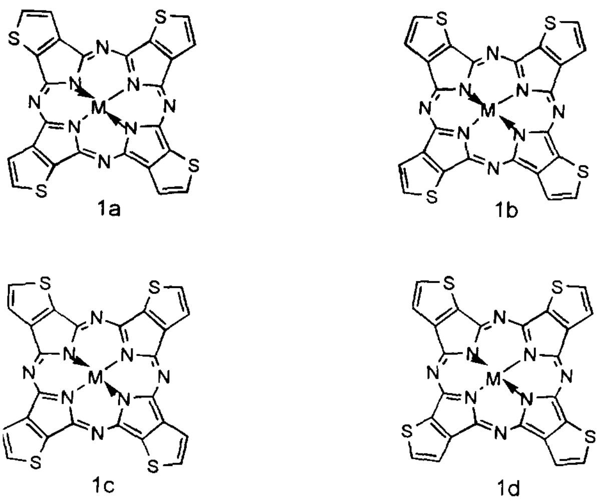
INTRODUCTION

Phthalocyanines as a chemical class provide the dominant blue and green pigments, due to their intense absorption at long wavelengths in the visible spectrum, to their excellent durability and their relatively low cost.[1-4] Certain phthalocyanine derivatives in which the intense absorption is shifted bathochromically into the near infrared region of the spectrum are of importance for a range of functional applications including optical data storage and security printing.[5] It is well-known that in typical donor–acceptor chromogens, such as azo dyes, the replacement of carbocyclic rings by five-membered heterocyclic rings, particularly those containing sulphur, can give rise to significant bathochromic shifts of the visible absorption band.[6] The effect on the absorption band in the electronic spectra of phthalocyanines of the replacement of the outer benzene rings by five-membered heterocyclic rings is less well established. In 1937, as part of Linstead's pioneering investigation into the chemistry of phthalocyanines, then a new chemical class of colourant, attempts to synthesise a series of analogues of phthalocyanine containing heterocyclic outer rings were reported,[7,8] although in the case of derivatives with five-membered rings with rather limited success. However, the isolation in low yield of the copper complex of tetrathieno[2,3-b]porphyrazine (**1**), the thiophene analogue of phthalocyanine, was reported. Attempts to prepare the metal-free analogue (**2**) were unsuccessful. In a subsequent paper, the electronic spectrum of the copper complex in 1-chloronaphthalene was reported although the investigation was limited by the capabilities of the instrumentation available at the time.[9] The spectrum was obtained quantitatively up to 640 nm and visual assessment was made in the wavelength region above that value. Absorption maxima at 593, 631 and 660 nm with progressively increasing intensities were reported and it was suggested tentatively that there was an absorption at an unspecified wavelength above 705 nm. More recently, Mitsubishi have patented a range of these compounds for use in optical recording.[10] In this paper, we describe the results of a further investigation of the chemistry of formation of tetrathieno[2,3-b]porphyrazines.

RESULTS AND DISCUSSION

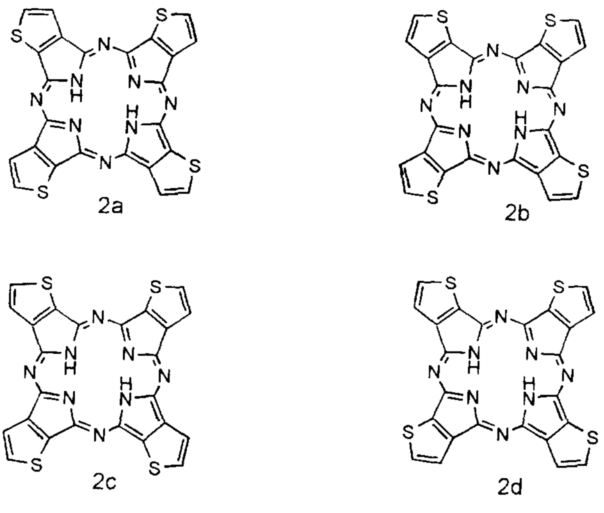
In a previous paper, we reported on the application of the PPP MO method, using a relatively simple but effective approach to parameterisation, to the prediction of the spectral properties of a range of substituted and benz-annulated phthalocyanines.[11] Subsequently, we have demonstrated that a good correlation may be obtained between the results of calculated and experimental UV/visible spectral data for a wide range of phthalocyanines.[12,13] The results of PPP MO calculations for each of the four possible geometric isomers (**a–d**) of the thiophene derivatives (**1**) and (**2**) using the structural models and parameterisation developed previously are given in Table 1. Absorption maxima with significant oscillator strengths for the longest wavelength bands of the isomers of the metal complexes (**1a–d**) are predicted in the range 663–701 nm, and for the metal-free derivative (**2a–d**) in the range 686–710 nm.

Linstead prepared the copper complex (**1**) from the reaction of thiophene-2,3-dicarbonitrile (**3**) with copper(I) chloride. His route to compound **3** from 3-methylthiophene is shown as route (a) in Scheme 1.[7] An alternative synthesis of compound (**3**) from thiophene, shown as route (b) in Scheme 1, has subsequently proved more efficient and worked well in our hands.[14] With a view to extending the range of available thiophene-2,3-dinitriles for the purpose of exploring substituent effects, we investigated the possibilities



1a 1b 1c 1d

1



2a 2b 2c 2d

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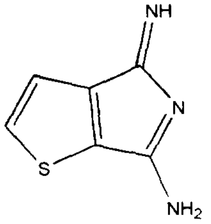
offered by the route illustrated in Scheme 2 from the readily available 2-aminothiophene-3-carbonitriles (**4a–c**). This route involves diazonium salt replacement reaction to form the iodo derivatives (**5**) followed by conversion to the dinitriles by treatment with copper(I) cyanide. Compounds (**6a**) and (**6b**) were prepared successfully via the iodo compounds (**5a**) and (**5b**) by this



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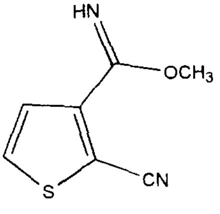

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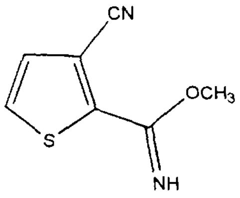

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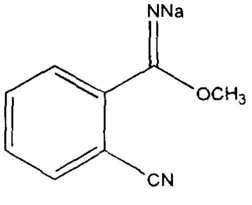

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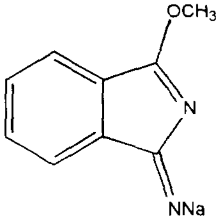

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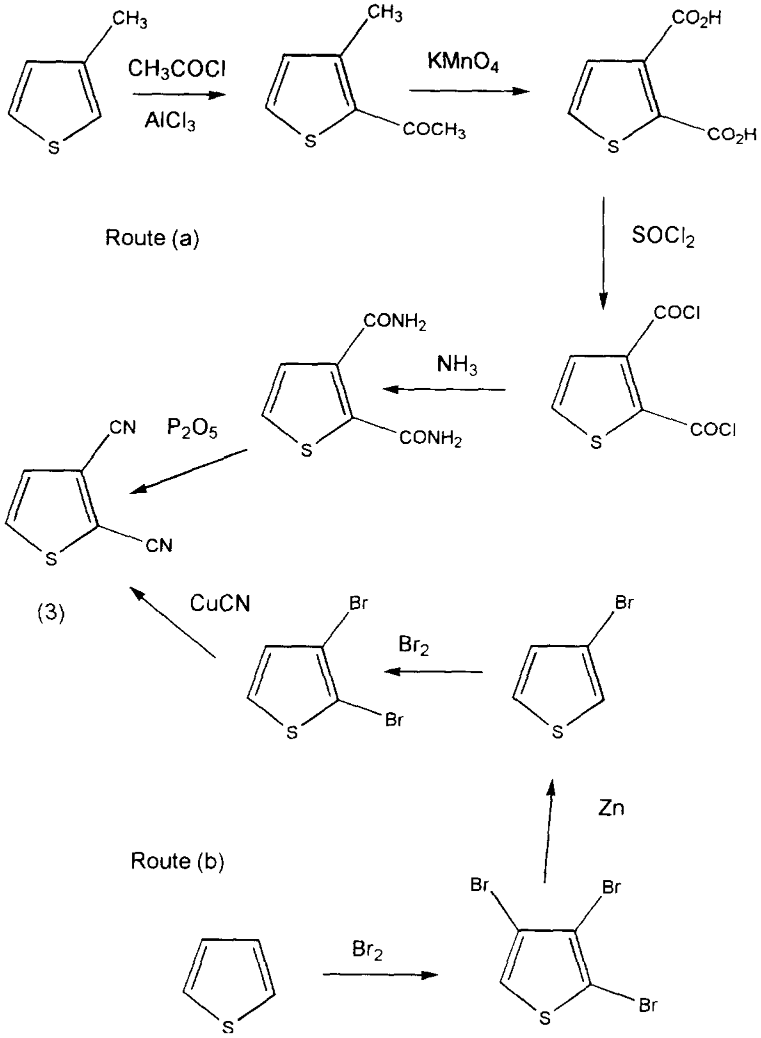
TABLE 1
Results of PPP MO Calculations for Metal-free Tetrathieno[2,3-b]porphyrazine (Isomers **2a–d**) and its Metal Complexes (Isomers **1a–d**)

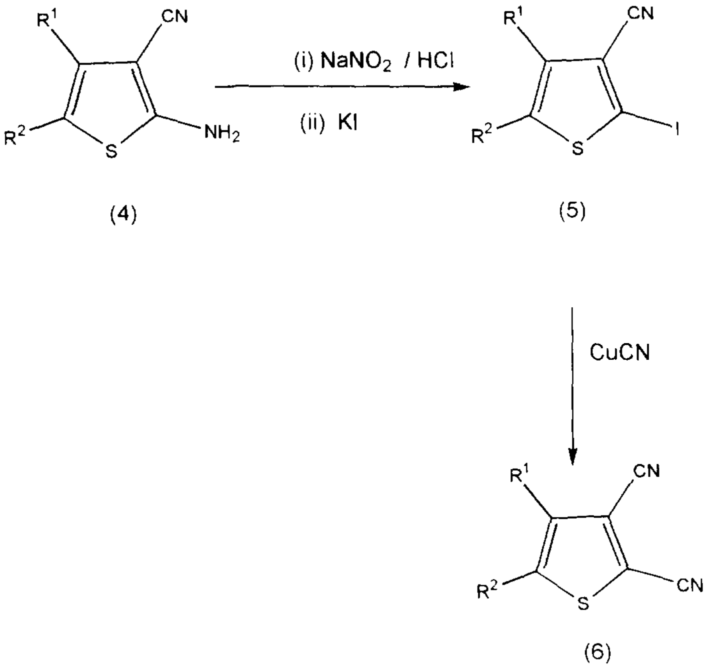
Isomer	*λ_{max}/nm (PPP calc) (f_{osc})*			
	1		**2**	
a	663 (1.04)	662 (1.55)	694 (1.47)	615 (0.96)
b	660 (1.62)	650 (1.02)	686 (1.56)	605 (0.94)
c	672 (1.58)	663 (0.89)	705 (1.49)	615 (0.84)
d	701 (1.03)	668 (1.48)	710 (1.41)	620 (1.02)
Average	674 (1.45)	661 (1.10)	699 (1.48)	614 (0.94)



Scheme 1

method, although in modest yield. Attempts to prepare compound **3** by this route were unsuccessful due to difficulties encountered in the attempted diazotisation of compound (**4c**), probably due to competing C-nitrosation at the 'exposed' 5-position on the thiophene ring.[15]

Aromatic *o*-dicarbonitriles may be converted directly into metal-free phthalocyanines in a variety of ways.[4] However, like Linstead, we were unsuccessful in attempts to prepare metal-free tetrathieno[2,3-b]porphyrazine (**2**) directly from the dinitrile (**3**). We chose therefore to attempt the synthesis of the aminoiminoisoindoline analogue (**7**), since conversion of



	R^1	R^2
a	$-(CH_2)_4-$	
b	H	NO_2
c	H	H

Scheme 2

such compounds into metal-free phthalocyanines is often relatively straightforward.[12,16] However, prolonged treatment of compound (**3**) with ammonia and sodium methoxide in methanol, under conditions which might have been expected to lead to compound **7**, instead gave the imidate ester (**8a**). Compound (**3**) has been reported to react with methanol in acidic media to give a mixture of isomers (**8a**) and (**8b**). In our case, which involves basic conditions, the product isolated was confirmed as isomer (**8a**) by comparison of its spectral data with those previously reported.[17] This reaction may be explained by nucleophilic addition of the methoxide ion to the cyano group, generally accepted as the first step in the formation of aminoiminoisoindolines, but in this case, even using forcing conditions, only compound **8a** was isolated and no reaction with ammonia was observed. Borodkin reported the isolation of imidate ester salt (**9**) from the reaction of phthalonitrile with sodium methoxide in refluxing benzene, and when the same reaction was carried out in methanol, ring-closure to give the isoindoline salt (**10**) was observed.[18] Prolonged heating in refluxing methanol converted both (**9**) and (**10**) to disodium phthalocyanine, from which metal-free phthalocyanine may be obtained.[18] However, attempts to convert compound (**8a**) to tetrathieno[2,3-b]porphyrazine (**2**) in a similar way even using long reaction times and high reaction temperatures were unsuccessful, resulting only in recovery of the starting material.

A range of conditions for the conversion of compound (**3**) into the copper complex of tetrathieno[2,3-b]porphyrazine (**1**) were investigated. However, even using the optimum conditions, which involved treatment with copper(II) acetate in refluxing 1-chloronaphthalene for 1 h, we found, as did Linstead in his earlier work,[7] that yields were low and only reasonable analytical data could be obtained. In a similar way, we were able to obtain cobalt, vanadyl and lead derivatives of compound (**1**) as blue solids, although again not in analytically pure form. The infrared spectra of the complexes showed absorptions characteristic of phthalocyanine analogues. For example, the spectrum of the copper complex showed peaks which may be attributed to C–H stretching vibration (3054 cm^{-1}), C–C stretching and aromatic ring vibrations (1514, 1424, 1257 cm^{-1}) and C–H deformations (1160, 742 cm^{-1}). The electronic spectra of the metal derivatives of tetrathieno[2,3-b]porphyrazine (**1**) show features characteristic of the spectra of metal phthalocyanines,[11] in each case giving a single strong absorption band at long wavelengths, with two weaker absorptions at shorter wavelengths which are probably vibrational in origin. The λ_{max} values are given in Table 2. The position of the absorption bands in the spectrum of the copper complex are consistent with those given by Linstead, but his suggestion that there might be an absorption band at higher wavelengths is incorrect.[9] The order of bathochromicities of the main absorption band in the spectra of the four metal derivatives of compound (**1**) (Pb > VO > Cu > Co) is the same as shown by the corresponding phthalocyanine derivatives (also given in Table 2). In

TABLE 2
λ_{max} Values (nm) from the Electronic Spectra in 1-Chloronaphthalene of some Metal Phthalocyanines (MPc)[13] and the Corresponding Thiophene Analogues (**1**)

M	*MPc*	**1**
Co	672, 607	652, 630sh, 588
Cu	678, 648, 610	657, 632sh, 594
VO	701, 675, 631	674, 652sh, 609
Pb	714, 680, 643	685, 662, 619
PPP (calc)	693	674[a]

[a] Average of the calculated values of the longest wavelength band for isomers **1a–d**.

each case, the tetrathieno[2,3-b]porphyrazine complexes are 20–30 nm hypsochromic of the corresponding metal phthalocyanines. It is of interest that, if the average values for the four possible isomers (**1a–d**) are considered, this hypsochromic shift is correctly predicted by the PPP MO calculations (Tables 1 and 2).

Attempts to convert substituted thiophene-2,3-dinitriles (**6a**) and (**6b**) to metal complex phthalocyanine analogues were unsuccessful, in each case leading only to small amounts of rather intractable black materials which did not exhibit any phthalocyanine-like behaviour.

CONCLUSION

It was not possible to synthesise metal-free tetrathieno[2,3-b]porphyrazine (**2**) from thiophene-2,3-dinitrile (**3**). Attempts to synthesise the 1-amino-3-iminoisoindoline (**7**) were unsuccessful, resulting instead in the formation of the imidate ester (**8a**) which resisted attempts at ring-closure reactions. Copper, cobalt, vanadyl and lead complexes of tetrathieno[2,3-b]porphyrazine (**1**) show typical phthalocyanine-like electronic spectral properties, shifted 20–30 nm hypsochromically with respect to the corresponding metal phthalocyanines, an effect correctly predicted by PPP MO calculations.

EXPERIMENTAL

Instrumental methods

Melting points are peak temperatures determined using a Mettler DSC12E Differential Scanning Calorimeter. Infrared spectra were recorded as KBr discs with a Perkin–Elmer 1740 Fourier Transform spectrometer. UV/visible spectra were recorded on a Perkin–Elmer Lamda 2 spectrophotometer from solutions in 1-chloronaphthalene. ^{1}H NMR spectra were recorded on a Perkin–Elmer R32 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 50 MHz. C, H and N analyses were carried out in the Department of Applied Chemical Sciences, Napier University, Edinburgh. Mass spectra were recorded on a Kratos MS9 double-focusing, forward geometry mass spectrometer.

PPP molecular orbital calculations

A standard PPP MO procedure was used within the fixed β approximation.[19] The structural models and the parameters for the phthalocyanine ring system were as previously reported.[11–13] Literature values for the parameters for the heterocyclic sulphur were used.[20] Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship.[21]

Synthesis

*2-Aminothiophene-3-carbonitriles (**4a–4c**)*

2-Amino-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**4a**) was prepared from cyclohexanone, sulphur and malononitrile by the method of Gewald.[22] 2-Amino-5-nitrothiophene-3-carbonitrile (**4b**) was prepared from compound (**4c**) by formylation, nitration and deformylation according to literature procedures.[23] 2-aminothiophene-3-carbonitrile (**4c**) was prepared from malonitrile and 1,4-dithiane-2,5-diol by literature procedures.[23]

*2-Iodothiophene-3-carbonitriles (**5a**) and (**5b**)*

Sodium nitrite (0.38 g, 0.0055 mol) was added to concentrated sulphuric acid (3 cm^3) and the mixture then heated to 70°C for 10 min prior to cooling in an ice/salt bath to 0°C. A mixture of water (1 cm^3) and acetic acid (4 cm^3) was then added dropwise over a period of one hour, whilst maintaining a temperature of 0°C. 2-Aminothiophene-3-carbonitrile (**4a**) or (**4b**) (0.0055 mol) was stirred in a mixture of water (2 cm^3) and acetic acid (3 cm^3) at room temperature for 1 h. Concentrated sulphuric acid (1.5 cm^3) was added to this mixture dropwise keeping the temperature below 25°C with external cooling. The resulting solution was cooled to 0°C and added to the nitrosylsulphuric acid solution over 10 min. The mixture was then kept at 0°C for 3.5 h. To the resulting diazonium salt solution was added a solution of potassium iodide (0.91 g, 0.055 mol) in water (5 cm^3), the resulting mixture allowed to reach room temperature and stirred for a further 16 h. The mixture was then diluted with water, extracted with dichloromethane (3×300 cm^3), the extracts washed with dilute aqueous sodium carbonate, dilute aqueous sodium metabisulphite and then dried over anhydrous magnesium sulphate. The products were obtained after evaporation of the extracts followed by chromatography using a silica column with dichloromethane as the eluant. The following compounds were obtained:

2-Iodo-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carbonitrile (**5a**), (0.42 g, 26%), was obtained as off-white crystals (from methanol) m.p. 86–87°C. δ_H ($CDCl_3$) 2.15 (4H, m, CH_2), 2.95 (4H, m, CH_2). δ_C ($CDCl_3$) 21.9, 22.8, 24.7, 24.9 (CH_2), 82.3 (CN), 115.2 (C-2), 120.5 (C-3), 138.3 (C-4), 143.4 (C-5). Found: C, 37.0; H, 2.7; N, 4.8%. C_9H_8NSI requires C, 37.4; H, 2.8, N, 4.8%. M^+ at m/e 289. ν_{max} 2940 (C-H str.), 2234 (CN str.), 470 (C-I str.)

2-Iodo-5-nitrothiophene-3-carbonitrile (**5b**) (0.42 g, 27%), was obtained as off-white crystals from methanol, m.p 137–138°C. δ_H ($CDCl_3$) 7.87 (1H, s, 4-H). δ_C ($CDCl_3$) 95.2 (CN), 113.5 (C-2), 120.3 (C-3), 129.3 (C-4), 156.1 (C-5). Found: C, 21.7; H, 0.3; N, 10.6%. $C_5HN_2O_2IS$ requires C, 21.4; H, 0.4, N, 10.1%. M^+ at *m/e* 280. ν_{max} 2928 (C-H str.), 2224 (CN str.), 1328 (NO_2 str.), 470 (C-I str.)

Thiophenedinitriles

Thiophene-2,3-dicarbonitrile (3). 3-Bromothiophene was prepared from thiophene by the method of Gronowitz and Raznikiewicz.[24] Bromination of 3-bromothiophene by the method of Gronowitz[25] gave 2,3-dibromothiophene which was treated with copper(I) cyanide by the method of Paulmier *et al.*[14] to give thiophene-2,3-dicarbonitrile (**3**).

*Thiophene-2,3-dicarbonitriles (**6a**) and (**6b**).* Copper(I) cyanide (0.28 g, 0.022 mol) was added to a solution of the 2-iodothiophene-3-carbonitrile (**5a**) or (**5b**) (0.002 mol) in 1,1,3,3-tetramethylurea (25 cm^3) and the mixture refluxed for 3 h. The mixture was cooled, poured into water (250 cm^3) and extracted with dichloromethane (3×150 cm^3). The extracts were washed with water, dried over anhydrous magnesium sulphate and evaporated. The products were obtained by flash chromatography using a silica column with dichloromethane as the eluant. The following compounds were obtained:

4,5,6,7-Tetrahydrobenzo[b]thiophene-2,3-dicarbonitrile (6a) (0.18 g, 47%) was obtained as off-white crystals from methanol, m.p. 82–83°C. δ_H ($CDCl_3$) 1.90 (4H, m, CH_2), 2.78 (4H, m, CH_2). δ_C ($CDCl_3$) 21.3, 22.3, 24.3, 25.2 (CH_2), 111.6 and 111.9 (CN), 113.6, (C-2), 119.4 (C-3), 138.4 (C-4), 145.8 (C-5). Found: C, 63.9; H, 4.3; N, 14.5%. $C_{10}H_8N_2S$ requires C, 63.8; H, 4.3, N, 14.9%. M^+ at *m/e* 188. ν_{max} 2944 (C-H str.), 2214 (CN str.).

5-Nitrothiophene-2,3-dicarbonitrile (6b) (0.05 g, 13%) was obtained as off-white crystals from methanol, m.p 102–104°C. δ_H ($CDCl_3$) 8.08 (1H, s, 4-H). Found: C, 21.7; H, 0.3; N, 10.6%. $C_5HN_2O_2IS$ requires C, 21.4; H, 0.4, N, 10.1%. M^+ at *m/e* 191. ν_{max} 3110 (C-H str.), 2213 (CN str.), 1333 (NO_2 str.).

Reaction of thiophene-2,3-dicarbonitrile (3) with ammonia and sodium methoxide in methanol

Compound (**3**) was treated with ammonia and sodium methoxide in methanol according to established procedures[12,16] in an attempt to prepare the 1-amino-3-iminoisoindoline analogue (**7**).

The dinitrile (**3**) (0.01 mol), sodium methoxide (0.1 g) and methanol (25 cm^3) were stirred together at room temperature for 1 h while bubbling a rapid stream of anhydrous ammonia through the system. The temperature was raised to reflux with continued passage of ammonia for 3 h. The white solid which crystallised was filtered and chromatographed on a column of silica using dichloromethane as eluant. Compound (**8a**) was obtained (0.70 g, 42%) as white needles from methanol, m.p. 70–71°C. δ_H ($CDCl_3$) 3.96 (3H, s, CH_3), 7.32 (1H, d, 5-H), 7.51 (1H, d, 4-H), 8.52 (br s, NH). δ_C ($CDCl_3$) 53.8 (CH_3), 109.8, 114.2 (CN, C=NH), 128.9, 130.3, 143.0, 159.4 (ring C atoms). Found: C, 50.5; H, 3.5; N, 16.7%. $C_7H_6N_2OS$ requires C, 50.6; H, 3.6, N, 16.9%. M^+ at *m/e* 166. ν_{max} 3450 (N-H str) 3352, 3099 (C-H str.), 2229 (CN str.).

Metal tetrathieno[2,3-b]porphyrazines (1)

Thiophene-2,3-dicarbonitrile (0.67 g, 0.005 mol) and the appropriate metal salt (0.00125 mol) were refluxed in 1-chloronaphthalene (10 cm^3) for 1 h. The mixture was cooled, poured into acetone (50 cm^3) and the blue product filtered, washed with hot acetone and dried. The following complexes (**1**) were obtained as blue–green solids:

Copper complex (0.12 g, 16%) [from copper(II) acetate]: found C, 45.3; H, 1.8; N, 17.2. $C_{24}H_8N_8S_4Cu$ requires C, 48.0; H, 1.3; N, 18.7%;

Cobalt complex (0.08 g, 10%) [from cobalt(II) acetate]: found C, 44.0; H, 1.6; N, 14.0. $C_{24}H_8N_8S_4Co$ requires C, 48.4; H, 1.4; N, 18.8%;

Lead complex (0.05 g, 6%) [from lead(II) acetate]: found C, 41.23; H, 1.1; N, 12.9. $C_{24}H_8N_8S_4Pb$ requires C, 47.7; H, 1.3; N, 18.6%;

Vanadyl complex (0.09 g, 12%) (from vanadyl chloride) found C, 41.3; H, 1.4; N, 14.9. $C_{24}H_8N_8S_4VO$ requires C, 47.7; H, 1.3; N, 18.6%.

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