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Extended Bis-Aryldithiolene Nickel Complexes: Near Infrared Absorbing Compounds

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ABSTRACT

Eleven new bis-aryldithiolene nickel complexes have been synthesised to examine their electronic absorbance properties. They include a new type of chromophore based upon extended bis-aryldithiolene nickel complexes incorporating either 1,2,4,5-tetrathiolbenzene, 1,2,4,5-tetrathiol-3,6-dichlorobenzene or 1,2,4,5-tetrathiol-3,6-difluorobenzene as a ligand. The new complexes based upon the tetrathiol ligand possessed broad near infrared absorbance at energies lower than those of previously reported metal dithiolenes.

1 INTRODUCTION

Bis-dithiolene nickel complexes have been known for some time.[1,2] Interest in these materials was originally stimulated by the bonding characteristics of these square-planar complexes.[3] More recently interest has been attracted by the potential technological application of their near infrared absorbing properties. This paper describes modifications made to the basic structure of the bis-aryldithiolene nickel complexes and which have resulted in new materials with interesting properties.

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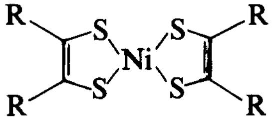
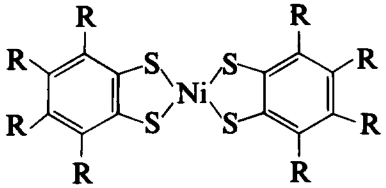
2 RESULTS AND DISCUSSION

The dithiolene complexes of the type I and II are known.[1] They can be made with oxidation states of 0, −1 or −2. The most stable form is dependent upon the electronic characteristics of the substituents R.



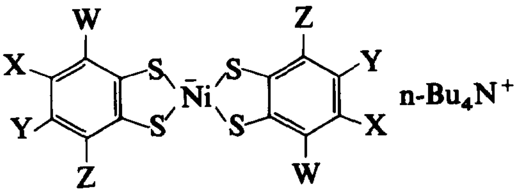
TYPE I R = Alkyl, Aryl, Nitrile



TYPE II R = Hydrogens, Halogens, Alkyl

A detailed description of the bonding present in these structures has been presented by Schrauzer.[3] Of note in this is the low energy separation of the $2b_{1u}$ and the $3b_{2g}$ orbitals, a predominantly ligand based orbital set. In the zero and −1 charged complexes of type I or II, the $3b_{2g}$ orbital is the lowest unoccupied orbital. An allowed inter-π transition from the $2b_{1u}$ to the $3b_{2g}$ orbitals results in the near infrared absorbance properties of these materials. The consequences of the ligand based structure of these orbitals is a sensitivity of the energy separation, and thus the frequency of the near infrared absorbance, to the inductive electronic effects of the substituents R. Hypsochromic shifts in the near infrared absorbance band are the result of electron-withdrawing substituents, and bathochromic shifts the result of electron-donating substituents. We have explored this effect by the synthesis of compounds **4** and **5**, and have further studied the effects of increased conjugation **6** and **7**, heterocycles **7** and **8**, and the fused dithiolene chromophores **9**–**14**.

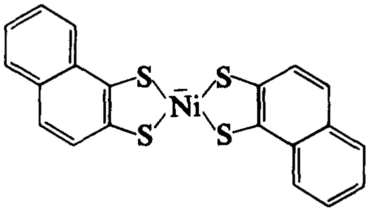
The bis-dithiolene complexes **4**–**14** were synthesised from their dithiol precursors using the general methodology of air oxidation in the presence of nickel dications and tetra-butylammonium. The reaction proceeds via the dianion which in all cases, except **7**, was unstable to oxygen and was transformed into the monoanion isolated as the tetra-butylammonium salt. The 1,2-dithiols were prepared from 1,2-dichloroaryl precursors by nucleophilic substitution with sodium hydrosulphide,[2,4–6] except for 1,2-dithionaphthalene which was made from 2-amino-1-nitronaphthalene. The



Compounds 1–5

Compounds 1–5

Compound	W	X	Y	Z
1	H	H	H	H
2	CH_3	CH_3	CH_3	CH_3
3	Cl	Cl	Cl	Cl
4	H	NO_2	H	H
5	H	NHAc	H	H



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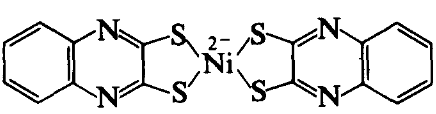

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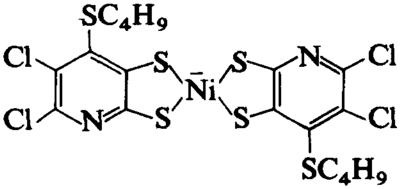

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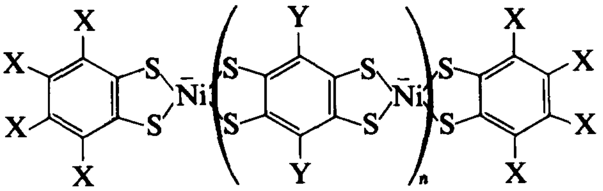
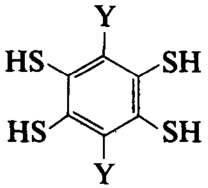


TYPE III Compounds **9–14**

Compounds 9–14

Compound	X	Y	n
9	Cl	H	1
10	Cl	Cl	1
11	Cl	F	1
12	F	F	4
13	F	F	5
14	Cl	Cl	9



Compounds **15–17**

Compounds 15, 16 & 17

Compounds	Y
15	H
16	Cl
17	F

three tetrathiols **15**, **16** and **17** were prepared in a similar way to the dithiols from the corresponding perhalogenated precursors. These tetrathiols were not particularly stable to air and were used crude. The nickel complexes were purified by recrystallisation or reprecipitation from chloroform/ethanol mixtures and structures assigned on the basis of mass spectra, electronic absorbance spectroscopy and compositional analysis. The peak maxima for the lowest energy absorbance band of compounds **1–14** are given in Table 1.

TABLE 1

Compound	*Charge*	*Peak max. (nm)*	*Extinction coefficient*	*Solvent*
1	−1	884	13 200	Dichloromethane
2	−1	926	16 400	Dichloromethane
3	−1	870	13 900	Chloroform
4	−1	830	[a]	Chloroform
5	−1	930	[a]	Chloroform
6	−1	977	12 400	Chloroform
7	−2	540	12 200	Dichloromethane
8	−1	330	[a]	DMF
9	−2	1 240	61 500	DMF
10	−2	1 210	60 000	DMF
11	−2	1 190	59 300	DMF
12	−5	1 650	177 500	DMF
13	−6	1 700	[b]	DMF
14	−10	1 900	[b]	DMF

[a] Exact values not available, but >10 000.
[b] No values can be given, since these materials exist in solution as a mixture of oligomers. Approx. calculations indicate the values to be in excess of 200 000.

All the new compounds exhibited a strong absorbance in the near infrared, with the exception of the nitrogen-heterocyclic compounds **7** and **8**. The position of the near infrared absorbance band was, as expected, sensitive to substituents. Thus, comparison of the nitro derivative **4** and the amido derivative **5** confirms that electron donation leads to a bathochromic shift. Contrast also compound **2**. Increased conjugation in compound **6** results in a bathochromic shift compared to the parent **1**.

The most dramatic effect was observed in the compounds of structures **9**–**14** derived from the 1,2,4,5-tetrathiols. Thus, comparing compound **3** to compounds **9**, **10** and **11**, a bathochromic shift of 370–350 nm occurs. This shift to much lower energy can be yet further accentuated by inclusion of additional tetrathiol units to produce the extended ribbon-like chromophores of type III exemplified by compounds **12**, **13** and **14**. Compound **14** shows a particularly broad low energy absorbance at peak maximum approximately 1900 nm (Fig. 1).

The products of tetrathiols were found to be equilibrium mixtures of substances of type III with different values for n. Thus, if formally $n = 1$, there was evidence to suggest that products of $n = 0$ and $n = 2$ were also present. This is a dynamic equilibrium. Addition of quantities of nickel dications with either dithiol or tetrathiol would alter the ratio of the constituent complexes as observed by electronic absorbance spectroscopy. This effect

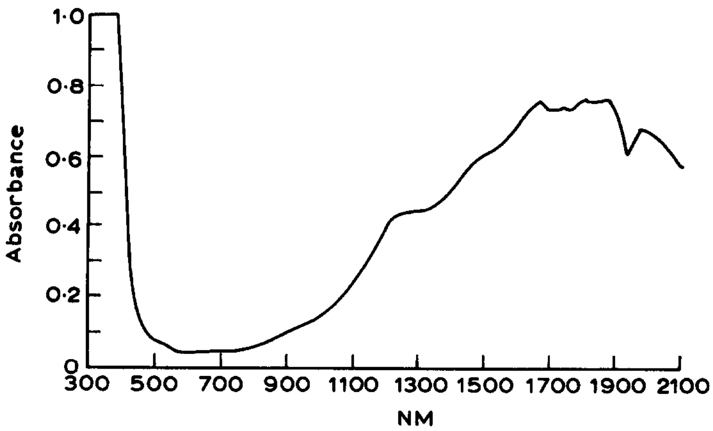


Fig. 1. Absorbance spectrum of compound **14** in DMF, at a concentration of 0·115 g/litre, path 0·1 cm.

was particularly evident for values of *n* > 5, for example compound **14** (Fig. 1). The very low energy of the electronic transition in this chromophoric system is lower than any previously reported metal dithiolene complex that we are aware of. This presents an intriguing question as to how far this effect can be pushed into the mid-infrared and what will be the electronic and redox properties of such substances.[7]

3 CONCLUSION

The near infrared absorbing properties of the bis-aryldithiolene nickel complexes can be modified to absorb at points over the range 830 to 2000 nm by appropriate choice of substituents. The effects of the 1,2,4,5-tetrathiols are remarkable in this and offer further opportunities for expansion of this absorbance range.

4 EXPERIMENTAL

4.1 Synthesis of 1,2-dithiols from 1,2-dichloroaryl precursors

The general process is exemplified below for the synthesis of 1,2,3,4-tetrachloro-1,2-benzenedithiol.

A mixture of hexachlorobenzene (57 g, 0·2 mol) and iron powder (6·27 g, 0·11 mol) in N,N-dimethylformamide (200 ml) was heated to 130°C. A mixture of powdered sodium hydrosulphide monohydrate (30 g, 0·4 mol) and sulphur (1 g, 0·03 mol) was added portionwise over 1 h. After 3 h the brown heterogeneous reaction mass was cooled to 60°C and diluted with water (400 ml). The precipitated solid was filtered and the filtrates discarded.

The residue was slurried in 50% aqueous methanol (200 ml) containing zinc oxide (8 g, 0·10 mol) and sodium hydroxide (20 g, 0·5 mol) and the mixture heated to reflux for 1 h, after which time it had changed from a dark brown acetone soluble product to a buff-coloured mixture, insoluble in acetone. The cooled mixture was filtered and the solid discarded. The filtrate was acidified with concentrated hydrochloric acid and the precipitated dithiol filtered. The product, a buff-yellow solid, was dried and used without further purification. The yield of solid was 45 g. Typically, the purity of the product was between 50% and 80%.

4.2 Synthesis of 1,2-dithiolnaphthalene

A mixture of 2-amino-1-nitronaphthalene[8] (31 g, 0·16 mol), sulphuric acid (100 ml) and sodium nitrite (13·8 g, 0·2 mol) was stirred for 2 h at below 10°C. After aqueous drown-out the recovered solid was added to a solution of sodium thiocyanate (67·4 g, 0·67 mol) and ferric chloride in ice/water (300 ml) and stirred overnight. The solid was recovered by filtration and dried. This material (5 g) was added to water (100 ml) containing hydrated sodium sulphide (10 g, 0·042 mol) and sodium hydroxide (8 g, 0·2 mol) and stirred for 30 min at 100°C. The cooled reaction mixture was acidified with concentrated hydrochloric acid and the precipitated product filtered and washed with water. This solid was heated in acetic acid (50 ml) with zinc (5 g) and concentrated hydrochloric acid (10 ml) at 95°C. After 30 min the mixture was filtered and poured into water (200 ml) and extracted with chloroform. The organic phase was dried over anhydrous magnesium sulphate and evaporated to dryness to give 1,2-dithiolnaphthalene (2·0 g, 6·2%).

4.3 General procedure for the synthesis of the dithiolene nickel complexes

The dithiol (2 mol. equiv.), nickel dichloride hexahydrate (1 mol. equiv.) and tetra-butylammonium bromide (or hydroxide, 1 mol. equiv.) were stirred in a mixture of N,N-dimethylformamide and tetrahydrofuran (1:1, 2 ml mmole^{-1}). Air was bubbled through the mixture for 3 h. The solvent was removed by rotary evaporation and the residue slurried in ethanol, filtered and then washed with ethanol and chloroform. The product was purified by reprecipitation from chloroform with ethanol and dried at 40°C. Yields were essentially quantitative based upon pure thiols.

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