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Syntheses and Characteristics of Infrared Absorbing 2:1 Nickel Complex Dyes

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SUMMARY

Some 2:1 nickel complex infrared absorbing dyes were synthesized by the reaction of phenylenediamines, 2-aminobenzenethiols and 2-aminobenzeneselenols with nickel(II) chloride. These dyes generally absorbed infrared light over 860 nm, but those from phenylenediamines absorbed at 780–800 nm, which is the most favorable wavelength region for semiconductor laser optical recording dye medium. Introduction of alkyl and/or amino groups into the parent dye greatly improved the solubility in organic solvent and these dyes could be applied by the wet coating method to prepare dye medium.

1 INTRODUCTION

There is a current interest in the development of near-infrared absorbing dyes which are used as the functional dyes for optical recording media and for protection in the optical filter. As gallium–arsenic (GaAlAs) semiconductor lasers with wavelengths of 800–830 nm are now being used as a light source for optical information-processing systems such as optical disk file equipment and laser beam printing, the dye media have to absorb light over 700 nm.[1] We have previously reported some naphthoquinones[2,3] and anthraquinones[4] which absorbed infrared light at 700–830 nm and had good properties as dye medium. Some dithiols have been described as metal

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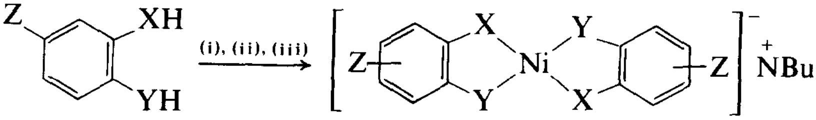
ion indicators[5] and can form 2:1 metal complexes which absorb in the infrared region, and some of them have been evaluated for possible use in optical recording media.[6] The dithiols are colorless, but their 2:1 metal complexes strongly absorb at 700–950 nm. The dithiol metal complexes also act as singlet oxygen quenchers and can be used to protect the photo-oxidation of the infrared dye of the optical memory disk.[7] In this paper, we report the syntheses of a new series of 2:1 nickel complex infrared dyes obtained from phenylenediamines and related compounds.

2 RESULTS AND DISCUSSION

2.1 Preparation of 2:1 nickel complex dyes

General procedures to prepare the 2:1 nickel complex dyes **1**–**3** are shown in Scheme 1. The reaction of toluene-3,4-dithiol with nickel(II) chloride in the presence of potassium hydroxide or potassium gave a green 2:1 nickel complex which was subsequently treated with tetra-*n*-butylammonium bromide to give to a cation-exchanged 2:1 nickel complex dye **1**. Dye **2** was prepared similarly from 2-aminobenzenethiol. Dye **3** was prepared by the metal exchange reaction of zinc 2-aminobenzeneselenate with nickel(II) chloride. Zinc 2-aminobenzeneselenate was prepared by the modified method described in the literature.[8]



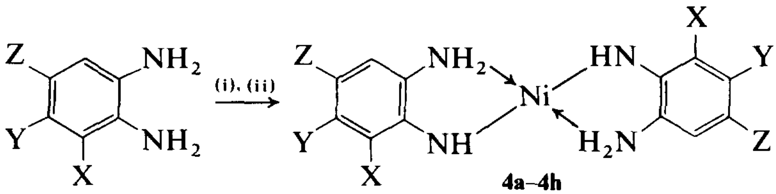
1–3

1 $X = Y = S$, $Z = CH_3$
2 $X = NH$, $Y = S$, $Z = H$
3 $X = NH$, $Y = Se$, $Z = H$

Scheme 1. (i) KOH or K; (ii) $NiCl_2 . 6H_2O$; (iii) $(n\text{-}C_4H_9)_4NBr$.

2.2 Preparation of 2:1 nickel complex dyes from phenylenediamines

The syntheses of the 2:1 nickel complex dyes were carried out by a method similar to that shown in Scheme 1 but the dyes obtained were not ionic, but neutral, as shown by their physical properties such as NMR spectra, TLC analysis and elemental analysis. The formation of these dyes **4a**–**4h** proposed is as shown in Scheme 2. It is proposed that the treatment of phenylenediamines with potassium hydroxide or potassium gives a



4a–4h

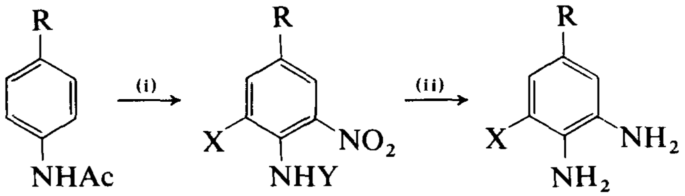
4a X = Y = Z = H
4b X = Z = H, Y = Me
4c X = H, Y = Z = Me
4d X = Z = H, Y = NO_2
4e X = Z = H, Y = Et
4f X = Z = H, Y = Bu
4g X = NH_2, Y = H, Z = Et
4h X = NH_2, Y = H, Z = Bu

Scheme 2. (i) KOH or K; (ii) $NiCl_2.6H_2O$.

monoanion and not a dianion, which then reacts with nickel(II) ion to give the neutral dye **4**. On the other hand, the formation of **1** is presumed to occur via the dianion reacting with the nickel(II) cation to give the dianion complex, which is subsequently oxidized by atmospheric oxygen to give the monoanion dye **1**.[9] The structural differences between **1–3** and **4** result in the dyes having different physical properties, especially in their absorption spectra.

The syntheses using phenylenediamine derivatives as ligands are shown in Scheme 3.

Introduction of the ethyl and butyl group and/or an amino group greatly improved the solubility in organic solvent and whilst dyes **4f–4h** dissolved readily in alcohol, dyes **1–3** and **4a–4e** showed only very slight solubility in solvents, except for dimethylformamide.



5a R = Et
5b R = Bu

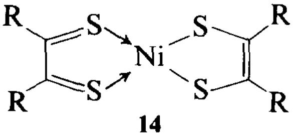
6a X = H, Y = Ac, R = Et
6b X = H, Y = Ac, R = Bu
7a X = NO_2, Y = Ac, R = Et
7b X = NO_2, Y = Ac, R = Bu
8a X = H, Y = H, R = Et
8b X = H, Y = H, R = Bu

9 X = H
10 X = NH_2

Scheme 3. (i) HNO_3/H_2SO_4; (ii) H_2/Raney-Ni.

2.3 Visible absorption spectra and some properties

It is well known that the 2:1 nickel dithiolene chromophores **14** form a square-planar structure with nickel as the central metal, and can give rise to near-infrared absorption at 700–900 nm. The intense absorption of **14** is clearly due to the π–π^* transition of 10π-systems.[10]

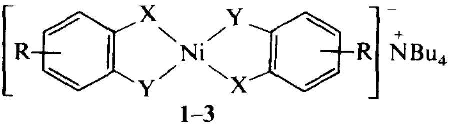
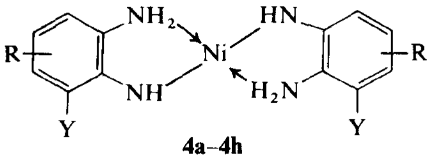


14

R = Me, $\varepsilon = 28\,200$
R = Ph, $\varepsilon = 30\,100$

The chromophoric system of **1–3** was concluded to be similar to that of **14**, but **1–3** was isolated as the monoanion of the tetra-*n*-butylammonium salt. The molar extinction coefficients (ε) of **1–3** were in the region of $(1{\cdot}2–1{\cdot}4) \times 10^4$ and were lower than that of **14**. Schrauzer[11] has reported that the λ_{max} of **14** changed depending on the oxidation stages; the dianion is colorless but the monoanion and neutral species are green. On the other hand, dyes **4** were isolated as neutral species and absorbed at 780–850 nm. The ε values of **4** were $(2{\cdot}5–5{\cdot}3) \times 10^4$ and were much larger than those of **1–3**. Large substituent effects on the ε values of **4** were observed. Thus, introduction of long alkyl groups and/or an amino group decreased the ε values. The absorption spectra of 2:1 nickel complex dyes are shown in Table 1 and typical absorption spectra of 2:1 nickel complex dyes are shown in Fig. 1.

TABLE 1
Absorption Spectra of 2:1 Nickel Complex Dyes[a]

Dye	*R*	*X*	*Y*	λ_{max} *(nm)*	$(\varepsilon \times 10^{-4})$
1  **1–3**	4-Me	S	S	890	(1·40)
2	H	NH	S	894	(1·20)
3	H	NH	Se	858	(1·42)
4a  **4a–4h**	H		H	783	(5·26)
4b	4-Me		H	790	(5·32)
4c	4,5-Me_2		H	806	(3·78)
4d	4-NO_2		H	844	(2·53)
4e	4-Et		H	794	(2·78)
4f	4-Bu		H	795	—
4g	5-Et		3-NH_2	790	—
4h	5-Bu		3-NH_2	795	(2·90)

[a] Measured in dimethylformamide in a concentration of 1×10^{-4} mol liter^{-1}.

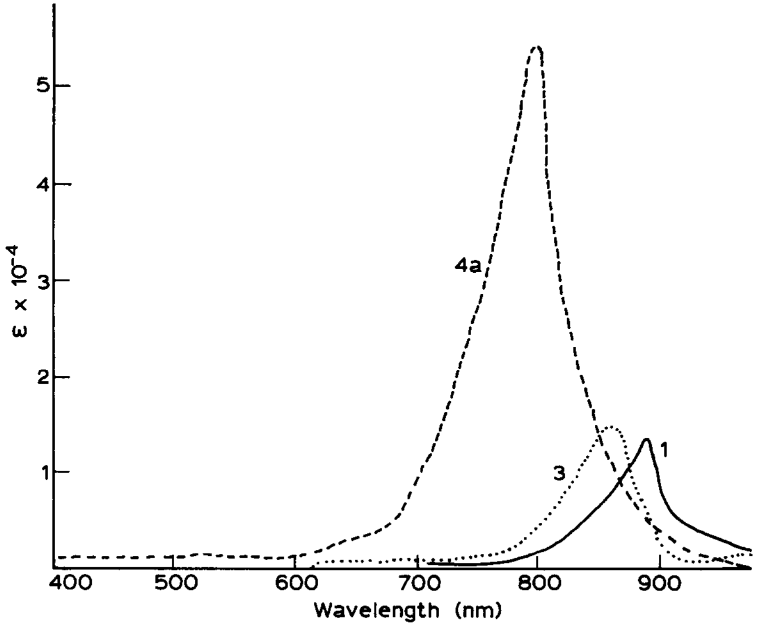


Fig. 1. Comparison of the absorption spectra of 2:1 nickel complex dyes **1** (——), **3** (-··-) and **4a** (– – –).

3 EXPERIMENTAL

The visible spectra were measured using a Shimadzu UV-240 spectrophotometer. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. The mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 70 eV.

3.1 Preparation of 2:1 nickel complexes (general method)

Toluene 3,4-dithiol (1 g, 6·4 mmol) was added to a solution of potassium (0·5 g, 12·8 g-atom) or potassium hydroxide (13 mmol) in 15 ml of absolute ethanol. An ethanol solution (15 ml) of nickel(II) chloride hexahydrate (0·74 g, 3·2 mmol) was added to the mixture, whereupon an intense green color appeared. Tetra-*n*-butylammonium bromide (2 g, 6·2 mmol) in 15 ml of absolute ethanol was added to the mixture, which was then allowed to stand for 2 h at room temperature with occasional stirring. The mixture was cooled in ice and the separated precipitate was filtered, washed with 2-propanol and ether, and then dried in air. The product was dissolved in 20 ml of warm acetone and filtered. The filtrate was concentrated under reduced pressure and 2-propanol was added to precipitate the complex. The product

TABLE 2
Properties and Characterization Data of Products

Compound	*Melting point (°C)*	*Yield (%)*	*Molecular formula*	*MS (M)*	*Analysis (%)*		
					C (calc.)	*H (calc.)*	*N (calc.)*
1	148–150	—[a]	$C_{30}H_{48}NS_4Ni$	—[b]	61·85 (62·32)	8·88 (8·72)	2·16 (2·02)
4a	>300	—[a]	$C_{12}H_{14}N_4Ni$	—[b]	52·88 (52·80)	3·84 (5·13)	20·16 (20·54)
4b	>300	—[a]	$C_{14}H_{18}N_4Ni$	—[b]	57·62 (55·87)	4·53 (5·98)	17·43 (18·62)
4c	>300	—[a]	$C_{16}H_{22}N_4Ni$	—[b]	58·03 (58·41)	6·29 (6·69)	14·89 (17·04)
4d	>300	—[a]	$C_{12}H_{12}N_5O_2Ni$	—[b]	40·92 (39·70)	2·17 (3·30)	21·18 (23·16)
4e	>300	—[a]	$C_{16}H_{22}N_4Ni$	—[b]	59·86 (58·76)	6·12 (6·73)	16·24 (17·14)
4f	>300	—[a]	$C_{20}H_{30}N_4Ni$	—[b]	63·85 (62·71)	7·43 (7·84)	14·42 (14·63)
5a	142–143	83	$C_{10}H_{13}NO$	163	73·53 (73·63)	7·82 (7·98)	8·90 (8·59)
6a	158	36	$C_{10}H_{12}N_2O_3$	208	57·23 (57·69)	5·92 (5·77)	13·24 (13·46)
7a	160–161	42	$C_{10}H_{11}N_3O_5$	253	47·08 (47·43)	4·38 (4·35)	16·65 (16·60)
5b	148–149	83	$C_{12}H_{17}NO$	191	75·60 (75·39)	8·27 (8·90)	7·02 (7·32)
6b	157	28	$C_{12}H_{16}N_2O_3$	236	61·28 (61·06)	6·92 (6·78)	12·01 (11·86)
7b	165	35	$C_{12}H_{15}N_3O_5$	281	51·08 (51·24)	5·92 (5·34)	15·32 (14·95)
8a	86	62	$C_8H_{10}N_2O_2$	166	57·68 (57·83)	6·08 (6·02)	16·82 (16·86)
8b	94	58	$C_{10}H_{14}N_2O_2$	194	61·65 (61·85)	7·02 (7·21)	14·62 (14·43)
11	142	76	$C_7H_4N_2O_2Se$	228	36·75 (36·84)	1·46 (1·75)	12·41 (12·28)
12	207	67	$C_{12}H_8N_2O_4Se_2$	404	35·92 (35·64)	2·10 (1·98)	6·72 (6·93)
13	253	52	$C_{12}H_{22}N_2Se_2Zn$	419	35·25 (35·36)	2·97 (2·97)	6·91 (6·88)

[a] The yields of crude products were 70–80%, but were 10–20% after purification.
[b] The mass spectra of the complex could not be determined.

was filtered, washed and dried. The crude material (0·56 g) was recrystallized twice from ethanol–acetone (3:1, v/v) to give 0·3 g of dark blue crystals.

Other nickel complexes were prepared by similar procedures. In the cases of phenylenediamines as ligands, the neutral dyes **4** were obtained.

3.2 4-Ethyl- and 5-ethyl-3-amino-1,2-phenylenediamine

4-Ethylaniline (10 g) in 5% aqueous hydrochloric acid (700 ml) was reacted with acetic anhydride (121 ml) in the presence of aqueous sodium acetate (97 g) in water (600 ml). The mixture was stirred at 5°C for 1 h. The separated product was collected by filtration, washed with water and recrystallized from ethanol to give **5a** in 83% yield. Compound **5a** (6·16 g, 0·0378 mol) in conc. sulfuric acid (41 g) was nitrated with the mixed acid [60% nitric acid (4·15 g) and conc. sulfuric acid (4·23 g)] at 5°C for 1·5 h. The mixture was poured into water and the resulting product was separated and washed with aqueous sodium carbonate to give **7a**. The 3-nitro compound **6a** was mainly obtained at the reaction temperature of 18°C. Hydrolysis of **6a** with sodium hydroxide was carried out under reflux for 2 h. The mixture was poured into water and neutralized with aqueous hydrochloric acid. The separated precipitate was filtered, washed with water and dried.

Compound **8a** in ethanol was hydrogenated at 60°C in the presence of Raney nickel (12 g) for 2 h in an autoclave. Solvent was evaporated under reduced pressure and the resulting amine was then reacted without further purification with nickel(II) chloride. Butyl analogs were synthesized using the same conditions (Scheme 3).

3.3 Preparation of zinc 2-aminobenzeneselenate (13)

o-Nitroaniline (13·8 g) in 60 ml of 18% aqueous hydrochloric acid was diazotized at 0–5°C with aqueous sodium nitrite (7 g). Potassium selenocyanide (14·4 g) was added to the solution and the mixture stirred for 0·5 h. The separated product was collected by filtration and washed with water to give *o*-nitrophenylselenocyanide (**11**) in 78% yield.

The selenocyanide (18·5 g) in ethanol (1000 ml) was hydrolyzed with 30% aqueous sodium hydroxide at 30°C for 1·5 h. The separated product was filtered, washed with ethanol and water to give *o,o′*-dinitrodiphenyldiselenide (**12**) in 67% yield. The diselenide (3 g, $7{\cdot}5 \times 10^{-3}$ mol) in acetic acid (60 ml) was reduced with zinc powder (9·8 g) under reflux for 0·5 h. The solution was cooled at 50°C, 18% aqueous hydrochloric acid (64 ml) added and the liquor filtered. The filtrate was neutralized with aqueous sodium acetate and the separated product was filtered and washed with water to give zinc 2-aminobenzeneselenate (**13**) in 98% yield. Some properties and characterization data of the products are summarized in Table 2.

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