Journal of the Korean Society of Dyers and Finishers
Vol. 3, No. 3, pp. 29~33 (1991. 9)

〈研究論文(學術)〉

Syntheses of Infrared Absorbing Nickel Complex Dyes

Sung Hoon Kim and Yong Jin Lim

Department of Dyeing and Finishing, College of Engineering, Kyungpook National University
(Received September 9, 1991)

적외흡수 니켈 착체색소의 합성

김성훈 · 임용진

경북대학교 공과대학 염색공학과
(1991. 9. 9 접수)

Abstract—Some ir absorbing nickel complex dyes were synthesized by the reaction of phenylene diamines, 2-aminobenzenethiols and 2-aminobenzene selenols, tetrathiols with nickel (II) chloride. These dyes absorbed ir light, but those from phenylene diamines absorbed at 780-800 nm which is the most favorable wavelength region for semiconductor laser optical recording 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 optical filter. As the gallium-arsenic (GaAlAs) semiconductor lasers with wavelengths of 800-830 nm are now being used as a light source for optical information-processing system such as optical disk file equipment and laser beam printing, the dye media have to absorb light over 700 nm.[1] Some dithiols have been known as a metal ion indicator[2] to form 2 : 1 metal complex which absorbs at infrared region, and some of them are evaluated as one of the candidates for optical recording media.[3] Interest in these materials was originally stimulated by the bonding characteristics of these square-planar complexes.

In this paper, we wish to report the syntheses of new series of nickel complex infrared dyes.

2. 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.

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

Toluene 3,4-dithiol (1g, 6.4 mmol) was added to a solution of potassium (0.5g, 12.8g-atom) or potassium hydroxide (13 mmol) in 15 m*l* of absolute ethanol. An ethanol solution (15 m*l*) of nickel (II) chloride 6 hydrate (0.74g, 3.2 mmol) was added to the mixture, whereupon an intense green color appears. Tetta-n-butylammonium bromide (2g, 6.2 mmol) in 15 m*l* of absolute ethanol was added to the mixture, and 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 m*l* of warm acetone and filtered. The filtrate was concentrated under reduced pressure and 2-propanol was added to precipitate the

complex. The product was filtered, washed and dried. The crude material (0.56g) was recrystallized twice from ethanol-acetone (3 :1 v/v) to give 0.3g of dark blue crystal. Other nickel complexes were prepared by similar procedures. In the cases of phenylenediamines as ligand, neutral dyes 4 were obtained.

2.2 Preparation of ligands

4-Methyl-1,2-dithiol, 2-aminobenzenethiol, phenylenediamine tetrathiols and its 4-methyl, 4,5-dimethyl and 4-nitro derivatives are commercially available.

2.3 4-Ethyl and 5-ethyl-3-amino-1,2-phenylenediamine

4-Ethylaniline (10g) in 5% agueous hydrochloric acid (700 m*l*) was reacted with acetic anhydride (121 m*l*) in the presence of aqueous sodium acetate (97g) in water (600 m*l*). The mixture was stirred at 5℃ 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 (6.16g, 0.0378 mol) in concentrated sulfuric acid (41g) was nitrated with the mixed acid (60% nitric acid 4.15g and concentrated sulfuric acid 4.23g) at 5℃ for 1.5 h. The mixture was pourd into water and the resulting product was separated and washed with aqueous sodium carbonate to give 7a. 3-nitro compound 6a was mainly obtained at the reaction themperature of 18℃. Hydrolysis of 6a with sodium hydroxide was carried out under reflux condition 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℃ in the presence of Raney nickel (12g) for 2 h in the autoclave. Solvent was evaporated under reduced pressure and the resulting amine was reacted with

Table 1. Some properties and identifications of products

Comp. no.	M.p. (℃)	Yield (%)	Mol. formula	MS M	Analysis (%)		
					C (Calc.)	H (Calc.)	N (Calc.)
1	148-150	—[a]	$C_{30}H_{18}NS_4Ni$	—[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]	$C_{12}H_{12}N_6O_2Ni$	—[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)	3.27 (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	$C_{12}H_{15}N_3O_{15}$	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 those were 10-20% after purification.
b) The mass spectra of complex could not be detected.

nickel (II) chloride without further purification. Butyl analogues were synthesized under the same conditions (Scheme 3).

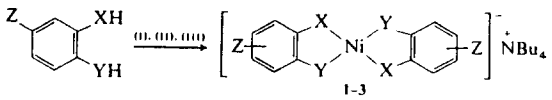
2.4 Preparation of zinc 2-aminobenzeneselenate, 13

O-nitroaniline (13.8g) in 60 ml of 18% aqueous hydrochloric acid was kept at 0-5℃ and was diazotized with aqueous sodium nitrite (7g). Potassium selenocyanide (14.4g) was added to the solution, and kept for 0.5 h. The separated product was collected by filtration, washed with water to give o-nitrophenylselenocyanide 11 in 78% yield. The selenocyanide (18.5g) in ethanol (1000 ml) was hydrolyzed with 30% aqueous sodium hydroxide at 30℃ for 1.5 h. The separated product was filtered, washed with ethanol and water to give o,o'-dinitrodiphenyl-diselenide **12** in 67% yield. The diselenide (3g, 7.5×10^{-3} mol) in acetic acid (60 ml) was reduced with zinc powder (9.8g) under reflux conditions for 0.5 h. The solution was cooled at 50℃, and 18% aqueous hydrochloric aicd (64 ml) was added and filtered. The filtrate was neutralized with aqueous sodium acetate. The separated product was filtered and washed with water to give zinc 2-aminobenzeneselenate 13 in 98% yield. Some properties and identifications of products are summarized in Table 1.

3. Results and Discussion

3.1 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 colored 2 : 1 nickel complex which was subsequently treated with tetra-n-butylammonium bromide to give 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 could be prepared by the modified method described in the literature.[4]



1-3

1, X=Y=S, Z=CH_3

2, X=NH, Y=S, Z=H

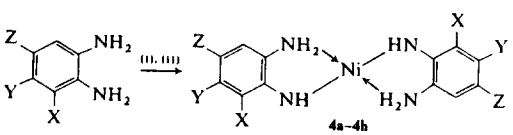
3, X=NH, Y=Se, Z=H

i, KOH or K; ii, $NiCl_2\cdot6H_2O$; iii, $(n\text{-}C_4H_9)_4NBr$.

Scheme 1.

3.2 Preparation of 2 : 1 nickel complex dyes from Phenylenediamines

Preparations of 2 : 1 nickel complex dyes were carried out by the similar method described in Scheme 1 but the obtained dyes were not ionic but neutral from their characterizations such as n.m.r. spectra, t.l.c. analysis and their identifications of elemental analysis. The formation of these dyes **4a-4h** were proposed as shown in scheme 2. It was proposed that the treatment of phenylenediamines with potassium hydroxide or potassium gave monoanion but not dianion which reacted with nickel (II) ion to give neutral dye **4**. While on the other hand, the formation of **1** was proposed that the dianion reacted with nickel (II) cation to give the dianion complex which was subsequently oxidized by atmospheric oxygen to give monoanion dye **1**.[5] The structural differences between **1-3** and **4** gave guite different physical properties expecially in their absorption spectra which were discussed in later sections. The syntheses of phenylenediamine derivatives as ligand were shown in Scheme 3.



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

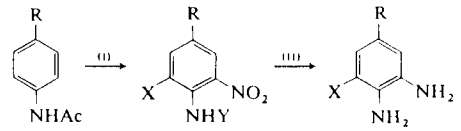
4f, X=Z=H, Y=Bu

4g, X=NH_2, Y=H, Z=Et

4h, X=NH_2, Y=H, Z=Bu

i, KOH or K; ii, $NiCl_2\cdot6H_2O$.

Scheme 2.



5a: R=Et
b: R=Bu

6a: X=H, Y=Ac, R=Et
b: X=H, Y=Ac, R=Bu
7a: X=NO_2, Y=Ac, R=Et
b: X=NO_2, Y=Ac, R=Bu
8a: X=H, Y=H, R=Et
b: X=H, Y=H, R=Bu
9: X=H
10: X=NH_2

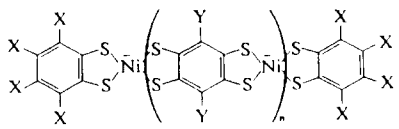
i. HNO_3/H_2SO_4; ii. H_2/Raney-Ni.

Scheme 3.

3.3 Preparation of nickel complex dyes from tetrathiols

Nickel complex dyes **14-19** were synthesized from their tetrathiol precursors using the general methodology of air oxidation in the presence of nickel dications and tetra-butylammonium.

Tetrathiols were not stable to air and were used crude. The nickel complex were purified by recrystallization or reprecipitation from chloroform ethanol mixtures and structures assigned on the basis of mass spectra, electronic absorbance spectroscopy and elemental analysis. All the new compounds exhibited a strong absorption in the near infrared.



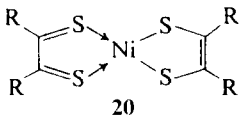
Dye **14-19**

Dye	X	Y	n
14	Cl	H	1
15	Cl	Cl	1
16	Cl	F	1
17	F	F	4
18	F	F	5
19	Cl	Cl	9

3.4 Visible absorption spectra and some properties

It is well known that the 2 : 1 nickel dithiolene chromophores **20** are formed a square-planar structure with nickel as central metal, and can give rise to near infrared absorption at 700-900 nm.

The intense absorption of **20** is clearly due to the π-π^* transition of 10π-system.[6]



20

R = Me, ε = 28 200
R = Ph, ε = 30 100

The chromophoric system of **1-3** was proposed as like as **20**, but **1-3** was isolated as monoanion of terta-n-butylammonium salt. The values molar extinction coefficient (ε) of **1-3** were 1.2-1.4$\times 10^4$ and were smaller than that of **20**. G. N. Schrauzer reported that the λ_{max} of **20** changed depending on their oxidation stages; dianion is colorless but monoanion and neutral species are green in color. On the other hand, dyes **4** were isolated as neutral species and absorbed at 780-850 nm. The ε values of **4** were 2.5-5.3$\times 10^4$ and were much bigger than those of **1-3**. The large substituent effects on the ε values of **4** were observed. Introduction of long alkyl groups and/or amino group decreased the ε values. The absorption spectra of nickel complex dyes were shown in Table 2 and typical absorption spectra of nickel complex dyes were shown in Fig. 1.

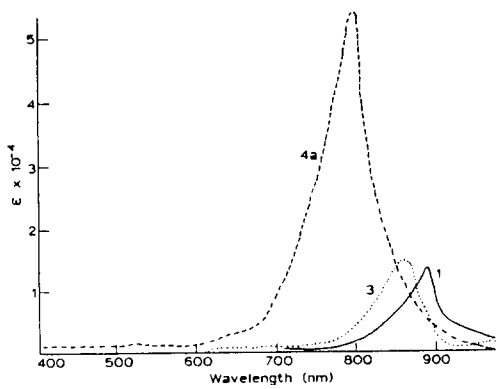
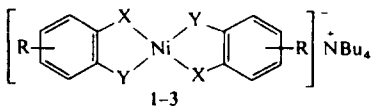
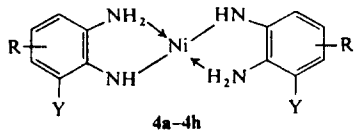
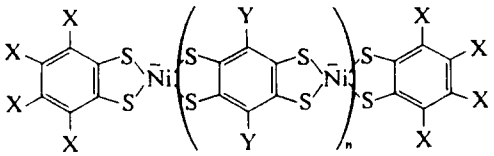


Fig. 1. Comparision of the absorption spectra of 2 : 1 nickel complex dyes 1 (—), 3 (-·-) and 4a (---).

Table 2. Absorption spectra of nickel complex dyes[a)]

Dye No.		R	X	Y	λ_{max} (nm)	($\varepsilon \times 10^{-4}$)
1		4-Me	S	S	890	(1.40)
2		H	NH	S	894	(1.20)
3		H	NH	Se	858	(1.42)
4a	1-3	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	4a-4h	4-Bu		H	795	–
4g		5-Et		3-NH_2	790	–
4h		5-Bu		3-NH_2	795	(2.90)
14			Cl	H	124	(6.15)
15			Cl	Cl	1210	(6)
16			Cl	F	1190	(5.93)
17			F	F	1650	(17.75)
18			F	F	1700	
19			Cl	Cl	1900	

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

References

1. M. Matsuoka, *Dyestuffs* and *Chemicals*, **30**, 308 (1985).
2. M. Kagiya, M. Yoshida, T. Akiyama and A. Sugimori, Nippon Kagaku Kaishi, 433 (1985).
3. Mitsuitoatsu Chemical Co Ltd., Japan Kokai, 57-11090.
4. H. Bauer, *Chem. Ber.* **46**, 92 (1912).
5. M. J. Baker-Hawkes, E. Billig, H. Harry and B. Gray, *J. Am. Chem. Soc.*, **5**, 4870 (1966).
6. J. Griffiths, *Shikizai Kyokaishi*, **59**, 485 (1986).