

Pronounced Hypsochromic Shift of Absorption Band and Improved Solubility of
Bis(1,2-diaryl-1,2-ethylenedithiolato)nickels. Prospective Near-IR Dyes
for Optical Data Storage

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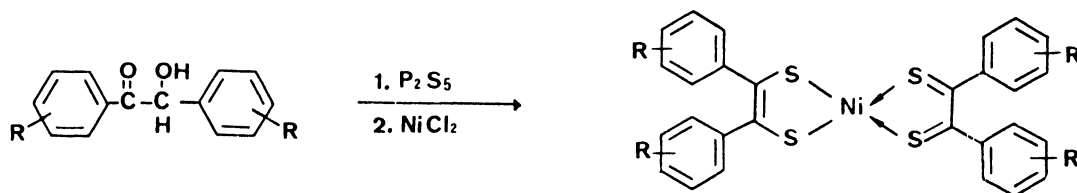
The introduction of halogen atoms at the 2-position in the benzene rings of bis(1,2-diaryl-1,2-ethylenedithiolato)nickel caused a pronounced hypsochromic shift of the absorption band in near-infrared region and improved the solubility to benzene. The nickel complexes with 2-halogen atoms are effective quenchers of singlet oxygen.

Interest in near-infrared absorbing dyes has been intense in recent years, since these dyes can be applied to organic colourants for the optical data storage using a Ga-As semiconductor laser diode.¹⁾ The organic colourants applied to this field have to have an absorption band in the near-infrared region (780-840 nm), same to oscillation wavelength region of a Ga-As laser diode. Their solubilities in appropriate organic solvents are also very important, as a recording thin layer is mainly formed by the spin-coating technique. A few of chromophoric systems have been modified to give properties as organic colourants for the optical disk memory system.^{1,2)}

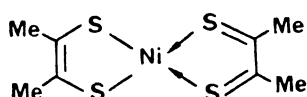
Though known nickel complexes such as 1a and 3 absorb in the near-infrared region, their absorption bands³⁾ are shifted to longer wavelength compared to the oscillation wavelength of the Ga-As laser diode. Recently, new bis(dithiolato)nickel complexes are prepared, but their absorption bands also are shifted to longer wavelength (> 900 nm).^{4,5)} Even if the nickel complex as 2 has absorption band at ca. 780 nm, its solubility to organic solvents is very poor. It is well known that 1a and 3 are efficient quenchers of singlet oxygen in the photofading process of dyes, in photo-oxidation process of plastics, and in oxidation of dimethylfuran.⁶⁻⁸⁾ In the optical data storage system, the nickel complex is mainly used as antioxidants,⁹⁾ not absorbers.

We now prepared the derivatives of 1 having sufficient solubility and the absorption band at ca. 780 nm, which fits the main oscillation wavelength of a Ga-As laser diode.

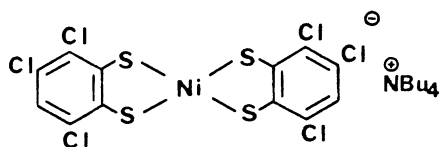
The nickel complexes (1) with various substituents were prepared from the corresponding benzoin derivatives by the Schrauzer's method,³⁾ and purified by column chromatography on silica gel using benzene as eluent or by recrystallization from benzene or n-hexane. In the mass spectrum, molecular ion (M^+) peak was observed and



1



2



3

- 1a: R=H
- 1b: R=4-CH₃
- 1c: R=4-OCH₃
- 1d: R=4-Cl
- 1e: R=4-CF₃
- 1f: R=3,4-(Cl)₂
- 1g: R=2-Cl
- 1h: R=2-Br
- 1i: R=2,4-(Cl)₂

other physical data were also satisfactory, supporting the structure of 1 (see Footnote 10). The intense absorption band in the near-infrared region of 1 is sensitive to substitution in the 4-position of phenyl group and is assigned to a $\pi-\pi^*$ ($2b_{1u} \rightarrow 3b_{2g}$) transition of ligands.^{2,11)} A good linear relationship exists between λ_{\max} and Hammett's modified substituent constants, σ_p^+ , of 1.¹²⁾ Substitution of hydrogens at the 4-position in phenyl groups of 1a with powerful electron-withdrawing groups caused a hypsochromic shift of the absorption band, i.e., 1e absorbs at 832 nm. However, further hypsochromic shift could not be achieved in this way.

On the other hand, the pronounced hypsochromic effect of the 2-halogen atom can be seen by comparison of 1a and 1g-1i. The nickel complexes with 2-halogen atoms showed an intense absorption band at ca. 780 nm (Table 1). The twist angles between the phenyl ring and five membered nickel chelate ring of 1a are 66° and 33°, respectively, confirmed by X-ray investigation.¹³⁾ The hypsochromic shift which caused by 2-halogen atoms in the phenyl groups of 1 suggests that the steric hindrance may increase the twist angles between the phenyl group and chelate ring, and decrease the conjugation between the chelate ring and the phenyl ring. This hindrance reduced the ϵ for 1g-1i to ca. $2.5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. In the resonance Raman spectra, the peak assigned to sulfur-nickel stretching vibration in the nickel complexes with 2-halogen atoms appeared at the lower frequency (378-385 cm^{-1}), compared with a corresponding value of 390 cm^{-1} in 1a in dichloromethane.¹⁴⁾

Comparison between the solubility of the pairs of 1d, 1g and 1f, 1i in benzene shows that the solubility is very effectively improved by introducing a halogen

Table 1. The absorption maxima in the near-infrared region and solubilities of nickel complexes 1 - 3

Ni complex	$\lambda_{\max}/\text{nm}^{\text{a)}$	$\epsilon \times 10^{-4}/\text{l mol}^{-1}\text{cm}^{-1}$	$\Delta\lambda/\text{nm}^{\text{b)}$	Solubility/wt% ^{c)}
<u>1a</u>	855	3.02	0	0.13
<u>1b</u>	877	3.17	+22	0.15
<u>1c</u>	894	2.80	+39	0.12
<u>1d</u>	861	3.54	+6	0.12
<u>1e</u>	832	2.99	-23	0.82
<u>1f</u>	850	3.10	-5	0.82
<u>1g</u>	783	2.56	-72	0.56
<u>1h</u>	783	2.52	-72	1.49
<u>1i</u>	787	2.23	-68	4.50
<u>2</u>	771	2.02	-	0.13
<u>3</u>	870	1.40	-	0.05

a) In CH_2Cl_2 . b) $\Delta\lambda = \lambda_{\max}(\text{substituted } \underline{1}) - \lambda_{\max}(\underline{1a})$. c) Solubility of the complex was determined in benzene at 25 °C.

atom to the 2-position of phenyl ring of 1. Compound 1i shows very sufficient solubility, compared with that of commercially available 3, together with an absorption band optimum for optical data storage.

With nickel complex 1i, as well as 1a, was found effective inhibition of photofading of Methylene Blue by singlet oxygen in the photoirradiation of the dye in the presence of oxygen.¹²⁾ These nickel complexes are effective inhibitors to the reported oxidation of dimethylfuran by singlet oxygen.¹⁵⁾ Thus, the relative conversions in photofading of Methylene Blue in the presence of nickel complex 1 after irradiation for 60 min were found as 48% (no quencher), 16% (1a), 14% (1g), 15% (1h), 16% (1i), and 6% (3), respectively. The relative percentages of the decrease in the peroxide formation of 2,5-dimethylfuran (no quencher: $1.2 \times 10^{-3} \text{ mol dm}^{-3}$) at $3.8 \times 10^{-5} \text{ mol dm}^{-3}$ of the quencher nickel complex were found as 0% (no quencher), 20% (1a), 15% (1d), 8% (1e), 3% (1f), and 18% (1i), respectively.

Therefore, nickel complex 1i will be a useful antioxidant and absorber for the optical disk memory system.

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- 10) Nickel complexes 1a-1e were previously prepared.¹²⁾ In the normal mass spectra, molecular ion (M^+) peak was observed. Spectral and microanalytical data of new compounds 1f-1i are as follows:
 - 1f: m/z 378 (33), 316 (100); RR (Resonance Raman spectra) $\nu_{S-Ni}^{CH_2Cl_2}$ 375, 400 cm^{-1} ; Anal. Found: C, 40.53; H, 1.68%. Calcd for $C_{28}H_{12}S_4Cl_8Ni$: C, 41.06; H, 1.48%.
 - 1g: m/z 678 (M^+ , 38), 432 (54), 303 (100); RR $\nu_{S-Ni}^{CH_2Cl_2}$ 378 cm^{-1} ; Anal. Found: C, 49.48; H, 2.21%. Calcd for $C_{28}H_{16}S_4Cl_4Ni$: C, 49.37; H, 2.37%.
 - 1h: m/z 854 (M^+ , 14), 640 (70), 638 (100) 636 (40); RR $\nu_{S-Ni}^{CH_2Cl_2}$ 378, 400 cm^{-1} ; Anal. Found: C, 39.33; H, 1.82%. Calcd for $C_{28}H_{16}S_4Br_4Ni$: C, 39.15; H, 1.88%.
 - 1i: m/z 816 (M^+ +2, 30), 814 (M^+ , 40), 798 (3.0) 796 (4.1) 378 (100); RR $\nu_{S-Ni}^{CH_2Cl_2}$ 310, 385 cm^{-1} ; Anal. Found: C, 41.72; H, 1.82%. Calcd for $C_{28}H_{12}S_4Cl_8Ni$: C, 41.06; H, 1.48%.
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