New Bis[3-(4′-dialkylaminophenylimino)pyrido[2,3-*a*]phenothiazine]nickel(II) Complexes with Near-infrared Absorptions

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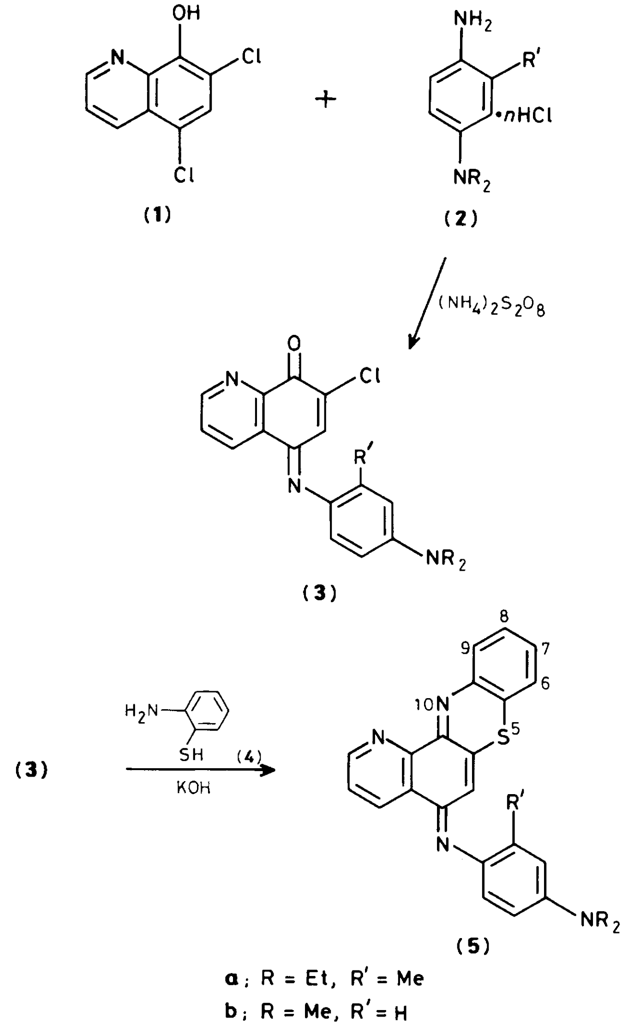
New nickel(II) complex dyes containing N,N-bidentate pyrido[2,3-*a*]phenothiazine-type ligands have been prepared; these dyes have an intense near-infrared absorption band in the range of 782—838 nm.

Recently, near-infrared absorbing dyes have attracted attention in the field of diode-laser optical storage.[1] However, few organic dyes which absorb at the diode-laser wavelength have been described. As a result syntheses of new corresponding functional dyes are of great interest. We have reported two new near-infrared absorbing metal-complex dyes with indoaniline-type ligands[2] and N,O-bidentate ligands of 6-substituted-quinoline-5,8-diones[3] which have good chemical properties for use in optical data storage. Here we report a new type of near-infrared absorbing nickel(II) complex dye containing the N,N-bidentate ligand, 3-(4′-dialkylaminophenylimino)pyrido[2,3-*a*]phenothiazine (**5**).

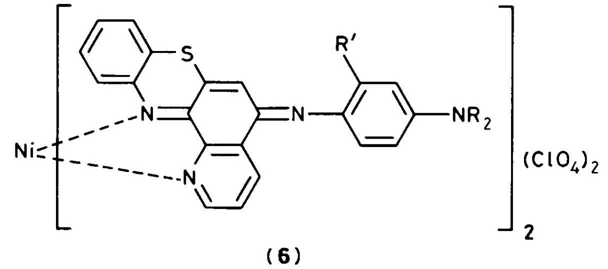
The free ligands (**5**) were prepared from 5,7-dichloro-8-hydroxyquinoline (**1**) as shown in Scheme 1. The precursors to (**5**), 5-(4′-dialkylaminophenylimino)-7-chloroquinolin-8-ones (**3**), were synthesized by condensing (**1**) with the dialkylaminoaniline hydrochlorides (**2**) in the presence of an oxidizing agent. A typical synthesis was as follows: to an aqueous NaOH solution of (**1**) (2.34 mmol) and (**2a**) (4.68 mmol), was added, dropwise, an aqueous solution of ammonium peroxydisul-



Scheme 1

phate (4.68 mmol) at 60 °C. The mixture was stirred for 10 min at 60 °C to give 5-(2′-methyl-4′-diethylaminophenylimino)-7-chloroquinolin-8-one (**3a**)† in 87% yield. Similarly, reaction of (**1**) with (**2b**) gave the corresponding dye (**3b**)† in 55% yield. These dyes (**3a**) and (**3b**) showed λ_{max} at 654 and 623 nm respectively in chloroform. The free ligands (**5a**) and (**5b**)† could be easily obtained in 54 and 52% yield, respectively, on the reaction of (**3a**) and (**3b**) with 2-aminothiophenol (**4**) (2 equiv.) in the presence of KOH under reflux for 10 min. Ligands (**5**) containing the strongly electron donating groups of the aniline moiety and phenothiazone ring were a new chromophoric system, and exhibited λ_{max} at 648 nm (**5a**) and 613 nm (**5b**) (chloroform).

Ligands (**5**) readily form chelate complexes in which a nickel(II) ion binds to the nitrogen of the pyridine moiety and N(10) as shown in structure (**6**). The absorption spectra of the free ligand (**5**) were affected by the addition of nickel(II) ion and showed a large bathochromic shift with an increase in molecular extinction coefficient. For example, for a 99% ethanol solution of (**5a**), addition of nickel(II) perchlorate hexahydrate resulted in the absorption maximum of 654 nm of (**5a**) decreasing and the growth of a new absorption band in the near-infrared region. A set of isosbestic points was observed at 555 and 700 nm. At a molar ratio of $[Ni^{II}]/[\mathbf{5a}]$ = 0.6, the absorption maximum at 654 nm disappeared completely, and a new absorption band (λ_{max} 838 nm, ε_{max} 54 400 l mol^{-1} cm^{-1}) was observed. The continuous variation method indicated the formation of a 1 : 2 nickel (II)–(**5a**) complex. A similar spectral change was observed in the complex formation of (**5b**) with nickel(II) perchlorate hexahydrate. Table 1 summarizes the spectral data for the free ligands (**5**) and their complex dyes (**6**). As shown in Table 1, the values of the red shifts, $\Delta\lambda_{max} = \lambda_{max}$ (complex) $- \lambda_{max}$ (free ligand), were 184 nm (**a**) and 166 nm (**b**), respectively, and the values of the molecular extinction coefficients of the complexes were found to be increased 4.9 (**a**) and 4.0 (**b**) fold compared with those of the free ligand.



(**6**)

a; R = Et, R' = Me
b; R = Me, R' = H

Table 1. Spectral data for the complex formation of $Ni(ClO_4)_2 \cdot 6H_2O$ with (**5**) in 99% EtOH.

		λ_{max}/nm (ε_{max}/l mol^{-1} cm^{-1})	
		a	**b**
Free ligand	(**5**)	654 (11 100)	616 (10 800)
Complex	(**6**)	838 (54 400)[a]	782 (43 600)[a]
$\Delta\lambda_{max}$[b]		184	166
$R\varepsilon$[c]		4.9	4.0

[a] Determined by spectral changes upon addition of $Ni(ClO_4)_2 \cdot 6H_2O$ in 99% EtOH. [b] $\Delta\lambda_{max} = \lambda_{max}$ (complex) $- \lambda_{max}$ (free ligand). [c] $R\varepsilon = \varepsilon_{max}$ (complex)/ε_{max} (free ligand).

The nickel(II) complex dye could be prepared in the following way: the reaction of (**5a**) (0.47 mmol) with nickel(II) perchlorate hexahydrate (1.18 mol) in ethanol–water solution under a nitrogen atmosphere for 30 min at room temperature gave the N,N-bidentate nickel(II) complex dye (**6a**), bis[3-(2′-methyl-4′-diethylaminophenylimino)pyrido[2,3-*a*]phenothiazine] nickel(II) diperchlorate,† in 97% yield. The absorption spectrum of the isolated 1 : 2 nickel(II) complex was in agreement with the spectral feature at $[Ni^{II}]/[\mathbf{5a}]$ = 0.6, the favourable absorption band for the main oscillation wavelength of a diode-laser. Similarly, another nickel(II) complex dye (**6b**)† was obtained in 95% yield, which has a strong absorption band in the near-infrared region. The syntheses of other corresponding metal complexes are under investigation and will be reported elsewhere.

These new complex dyes have applications for diode-laser optical storage media and optical filters. In addition, the free ligands showing a large bathochromic shift on complex formation can be used as a metal ion indicator.

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† The structure assignments were based on the observed analytical data.