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Dyes and Pigments, Vol. 35, No. 1, pp. 23–29, 1997

Printed in Great Britain
PII: S0143-7208(96)00091-5
0143-7208/97 $17.00+0.00

Synthesis and Characterization of Some Unsymmetric Substituted Bis(dithiobenzil)nickel Complex Dyes

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(Received 1 August 1996; accepted 10 September 1996)

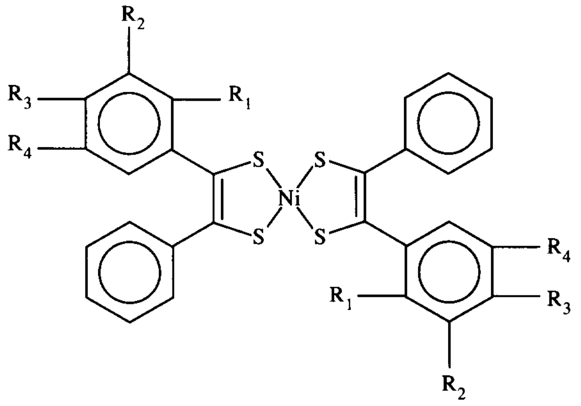
ABSTRACT

A new unsymmetric substituted bis(dithiobenzil)nickel complex containing two phenyl groups and two substituted phenyl groups was synthesized from a benzoin compound using phosphorus pentasulfide chloride. The benzoin compounds were prepared from phenylglyoxyal and substituted benzenes. The nickel complexes were characterized by elemental analysis, MS, ^{1}*HNMR and IR. The influence of substitutuents on the long wavelength absorption maxima of the nickel complexes was evaluated using the Hammett equation; they gave a pronounced effect relative to the corresponding symmetric nickel complexes, some of them having maximum absorption around 830 nm, and are thus very promising for use as near-infrared absorbing dyes for optical data storage using a Ga–As semiconductor laser diode. © 1997 Elsevier Science Ltd*

Keywords: bis(dithiobenzil)nickel complexes, organic recording media, near-infrared absorbing dyes, synthesis, optical data storage, characterization.

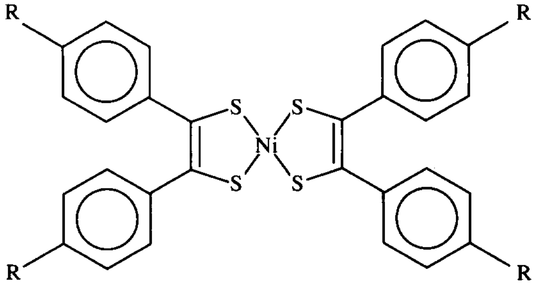
INTRODUCTION

Bis(dithiobenzil) nickel complexes are known to be effective in inhibiting the laser-induced fading of colored thin layers on recording disks, and have recently been applied in optical data storage systems together with near-infrared absorbing cyanine dyes [1, 2]. When these complexes are applied to an optical recording material using a semiconductor laser (wavelength: 830 nm), it is necessary to use one complex which has a maximum absorption in the vicinity of 830 nm. However, most symmetric nickel complexes containing the same four (un)substituted phenyl groups do not have suitable maximum absorption near 830 nm. This present paper reports the synthesis and characterization of a series of new unsymmetric substituted bis(dithiobenzil)nickel complexes containing two unsubstituted phenyl groups and two substituted phenyl groups (Formula **1**), and evaluates the substitutuent effect on the absorption of the complexes. We have also synthesized some symmetric substituted bis(dithiobenzil)nickel complexes containing the four same substituted phenyl groups (Formula **2**).



1

R_4	1a	1b	1c	1d	1e	1f	1g	1h	1i
R_1	H	H	H	H	H	H	H	CH_3	H
R_2	H	H	H	H	H	H	H	H	Br
R_3	H	$N(CH_3)_2$	OCH_3	CH_3	C_2H_5	Cl	$CH(CH_3)_2$	H	CH_3
R_4	H	H	H	H	H	H	H	CH_3	H



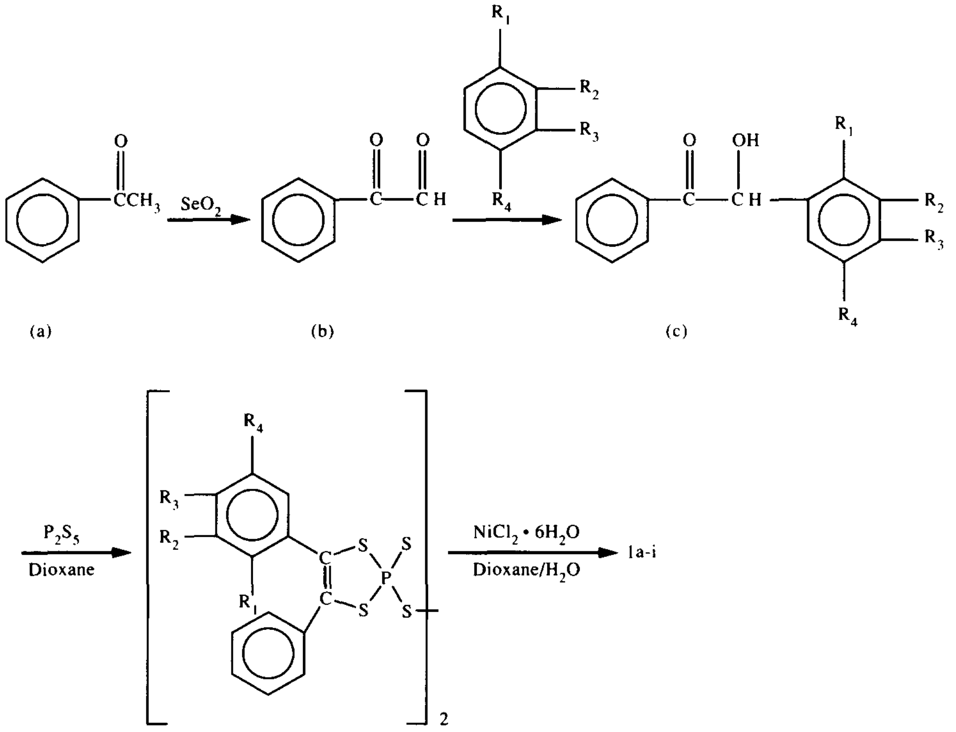
2a $R=OCH_3$
2b $R=CH_3$
2c $R=Cl$

2

RESULTS AND DISCUSSION

Preparation of unsymmetric bis(dithiobenzil)nickel complex

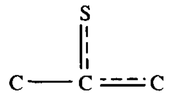
General procedures to prepare the nickel complexes **1c–i** are shown in Scheme 1. The bis(dithiobenzil)nickel complexes **1c–i** were prepared from the corresponding benzoin derivatives by the Schrauzer method [3]. The Benzoin derivatives (c) were synthesized by literature methods [4]. The general method for obtaining benzoin derivatives is the 'benzoin condensation', this method is normally suitable for symmetrically introducing substituent groups into both aromatic rings of the benzoin. However, the corresponding benzoin derivative for synthesizing the bis(dithiobenzil)nickel complexes of Formula **1** requires thepresence of substituent groups in only one of the two aromatic rings. Such a benzoin derivative can be synthesized by using both benzaldehyde and a substituted benzaldehyde. However, in this method, a reaction between the same type of benzaldehyde derivative inevitably takes place, and thus results in low yield problems. In this present paper, the benzoin derivative is synthesized by a method using phenylglyoxal, in view of its simplicity and good reaction yield (Scheme 1). Melting points, yields and analysis are summarized in Table 1.

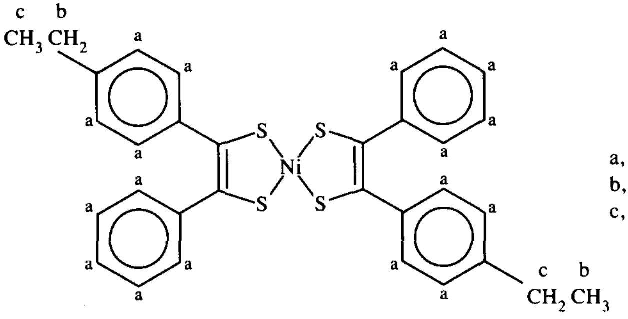


Scheme 1

Characterization

The structure of compounds **1c–i** was established by MS, IR and ^{1}H NMR (Tables 1 and 2). In the IR spectrum (Table 2) the 1356–1361 cm^{-1} band may be assigned to a vibration predominantly consisting of the perturbed C=C stretch, whereas the 1140–1142 cm^{-1} band corresponds to the perturbed C=S bond. The band at 883–884 cm^{-1} is tentatively assigned to a stretching vibration of the system. The ^{1}H NMR spectra provide chemical shift data in accordance with the structure of the nickel complexes. For example, the chemical shifts in ppm for the nickel complexes **1c–i** are shown below and in Table 2.





a, 6.98-7.60 (m, 18H)
b, 2.65 (q, 4H)
c, 1.25 (t, 6H)

TABLE 1
Properties and Characterization Data of New Nickel Complexes

Compound	*Melting Point (°C)*	*Yield (%)*	*Molecular Formula*	*Mass Spectra M$^+$*, m/z	*Analysis (%)* C *(calc.)*	*Analysis (%)* H *(calc.)*
1c	265	8.5	$C_{30}H_{24}O_2S_4Ni$	602	59.60 (59.71)	3.80 (3.96)
1d	260	25.0	$C_{30}H_{24}S_4Ni$	570	62.98 (63.05)	4.13 (4.23)
1e	250	17.5	$C_{32}H_{28}S_4Ni$	598	64.10 (64.18)	4.70 (4.71)
1f	245	15.6	$C_{34}H_{32}S_4Ni$	626	64.87 (65.07)	5.03 (5.14)
1g	245	5.5	$C_{28}H_{18}Cl_2S_4Ni$	611	54.80 (54.92)	2.92 (2.96)
1h	264	27.5	$C_{32}H_{28}S_4Ni$	598	64.12 (64.18)	4.58 (4.71)
1i	206	7.8	$C_{30}H_{22}Br_2S_4Ni$	726	49.61 (49.41)	3.12 (3.04)

TABLE 2
IR and ^{1}HNMR Spectroscopy Data of New Nickel Complexes

Compound	*IR Data (υ, cm^{-1})*	*^{1}HNMR Data (ppm)*
1c	1360, 12200, 752, 693	6.90–7.70 (m, 18H) 3.80 (s, 6H)
1d	1356, 1140, 884, 755, 695	7.20–7.60 (m, 18H) 2.35 (s, 6H)
1e	2950, 2864, 1358, 1140, 883, 755, 695	6.98–7.60 (m, 18H) 2.65 (q, 4H) 1.25 (t, 6H)
1f	1357, 1140, 1093, 884, 695	7.00–7.70 (m, 18H)
1g	2956, 2864, 1359, 1142, 884, 756, 693	6.90–7.70 (m, 18H) 2.90 (m, 2H) 1.25 (d, 12H)
1h	1363, 1147, 1114, 856, 754, 692	6.62–7.60 (m, 16H) 2.40 (s, 6H) 1.80 (s, 6H)
1i	1356, 1140, 755, 695	6.75–7.80 (m, 16H) 2.35 (s, 6H)

TABLE 3
Absorption Maxima in the Near-infrared of Nickel Complexes

Compound	*λ max^a (nm)*	*$\epsilon \times 10^{-4}$ ($l\ mol^{-1}\ cm^{-1}$)*	*$\Delta\lambda^b$ (nm)*
1a	855	3.02	0
1b	1050	2.86	195
1c	885	2.43	30
1d	870	3.86	15
1e	868	3.33	13
1f	856	3.68	1
1g	868	2.93	13
1h	835	1.89	−20
1i	860	3.55	5
2a	894	2.80	39
2b	877	3.17	22
2c	861	3.54	6

[a] Concentration: 1.0–2.0×10^{-5} M, in CH_2Cl_2.
[b] $\Delta\lambda = \lambda$max (**1b–i** and **2a–c**)−λmax (**1a**).

Electronic spectra

The absorption maxima in the near infrared region of the nickel complexes are shown in Table 3. In the symmetric substituted complexes, e.g. **2a–c**, the literature [5] has reported that a close linear relationship exists between the λmax values and the Hammett modified substituent constants, σ_p^+. In unsymmetric substituted nickel complex series, e.g. complexes **1b–f**, a non-linear relationship exists between the λmax values and the Hammett substituent constants, σ_p. However, when $(\sigma_p(X)+\sigma_p(H))/2$ is used as a substituent constant for the unsymmetric series, the correlation coefficient between $\Delta\lambda$max and the constants is 0.853 (Table 4 and Fig. 1). This shows that a reasonable linear relationship exists between the $\Delta\lambda$max values and the σ_p values for unsymmetric substituted nickel complexes. The absorption maxima of **1b–f** decreases in the order $N(CH_3)_2 > OCH_3 > CH_3 > C_2H_5 > Cl$. Compound **1b**, which contains a strong electron-donating substitutuent, has the longest λmax. Comparison of the absorption maxima of the pairs **1c** and **2a**, **1d** and **2b**, and **1f** and **2c**, shows that the unsymmetric nickel complexes have a pronounced effect relative to the corresponding symmetric nickel complexes. Some of the former, such as compound **1h**, which has maximum absorption in the vicinity of 830 nm, are thus very promising for use as near-infrared absorbing dyes for optical data storage using a Ga–As semiconductor laser diode.

General properties

Compounds **1c–i** have lower melting points with respect to the corresponding symmetric nickel complexes. They also have good solubility in organic solvents, and can be applied by the wet coating method to prepare the dye medium.

TABLE 4
Δλ of the Unsymmetric Nickel Complexes and σ_p

	$N(CH_3)_2$	OCH_3	CH_3	C_2H_5	Cl
$(\sigma_p(X) + \sigma_p(H))/2$	−0.32	−0.13	−0.085	−0.075	0.12
Δλ (nm)	195	30	15	13	1

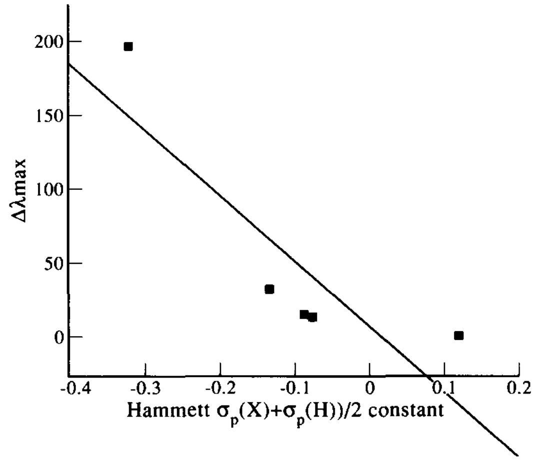


Fig. 1. Relationship between Δλ and Hammett $(\sigma_p(X) + \sigma_p(H))/2$ constants of substituent groups of the unsymmetric substituted nickel complexes.

EXPERIMENTAL

Instrumentation

Melting points were measured on a X4 micro-melting point apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer 683 spectrometer, visible/near-infrared spectra on a Hitachi UV-8451 A Spectrophotometer, mass spectra on a Finnigan 4021 and ^{1}HNMR Spectra on a Brucker Ac-200, using TMS as internal standard and chloroform-d as solvent.

Synthesis of bis(dithiobenzil)nickel complexes

The corresponding benzoin (1 equiv) was dissolved in 1,4-dioxane; phosphorous pentasulfide (3 equivs) was added and reacted for 2 hr under reflux. During this time the thiophosphoric esters of dithiobenzoin were formed and hydrogen sulfide was evolved. To the cooled and filtered reaction liquor an aqueous solution of nickel chloride hexahydrate (0.5 equivs) was added and the reaction mixture refluxed a further 2 hr. Black crystals of the complex were formed and collected by filtering the cooled solution. Purification was effected by extraction with boiling toluene or dichloromethane to give the required bis(dithiobenzil)nickel complex. These were then purified by column chromatography on silica gel using benzene as eluent, or by recrystallization from benzene. Relevant characterization data are given in Tables 1 and 2.

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