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The Syntheses and Crystal Structures of Some Bis(1,2-diaryl-1,2-ethylenedithiolato)nickel Complexes and their Photostabilising Efficiency to Organic Dyes

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ABSTRACT

The syntheses and properties of a series of compounds of general formula [(RCSCSR')$_2$Ni, R and R' = phenyl, substituted phenyl, condensed or heterocyclic rings] were studied. These complexes were prepared by reaction of symmetrical or asymmetrical benzoin derivatives (α-naphthoin, furoin and α-pyridoin) with phosphorus pentasulphide, and then with nickel chloride. The effect of the complexes on the photostabilisation of a quinophthalone dye was investigated in cellulose acetate films. It was observed that the films with these complexes, with the exception of the complex involving four furan rings in the symmetric ligand, showed excellent lightfastness relative to systems without the complexes. This stabilising function, based on singlet oxygen quenching, is discussed in connection with the crystal structure.

1 INTRODUCTION

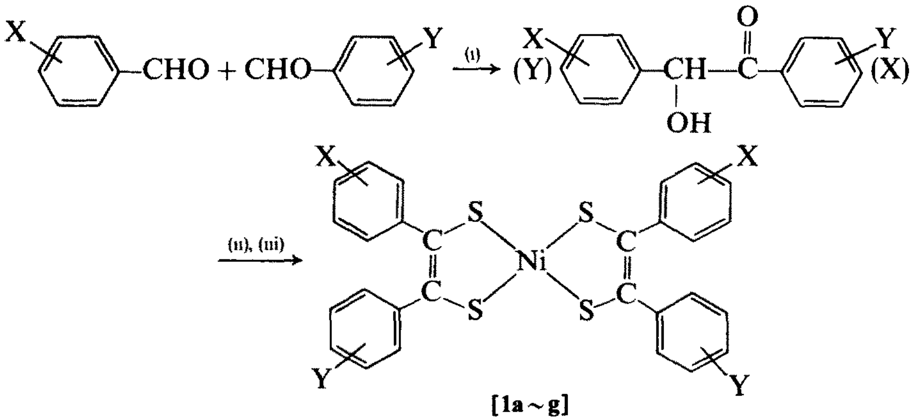
It is well known that bis(1,2-diaryl-1,2-diethylenedithiolato)nickel complexes act as quenchers of singlet oxygen, which is a principal contributor to the photodegradation of dyes in various substrates.[1-5] Recently, these nickel complexes have also been applied to optical data storage systems together with functional cyanine dyes and in which they act as antioxidants.[6] In these studies, bis(ethylenedithiolato)nickel complexes having phenyl or substituted phenyl rings were used and no complexes having condensed or heterocyclic rings were described.

In the present paper, the synthesis of some new bis(1,2-diaryl-1,2-ethylenedithiolato)nickel complexes having pyridine, furan or naphthalene rings is described. The effect of the new complexes on the photostabilisation of a quinophthalone dye in cellulose acetate films was investigated, together with compounds having symmetrical or asymmetrical phenyl rings. Additionally, the crystal structure of bis(dithiobenzil)nickel was analysed by X-ray diffractometer to study the stabilising mechanism.

2 RESULTS AND DISCUSSION

2.1 Preparation of bis(1,2-diaryl-1,2-ethylenedithiolato)nickel complexes with phenyl rings (1a–1g)

Nickel complexes, **1a**, **1c** and **1g**, with symmetrical phenyl rings were prepared from benzoin, 4-methoxybenzoin or 4,4′-diphenylbenzoin, by Schrauzer & Mayweg's method.[7] The preparation of asymmetrical nickel complexes having phenyl rings (**1b**, **1d–1f**) was carried out by a similar procedure using two types of substituted benzoin derivatives (which were obtained in ~85% yields from the corresponding aromatic benzaldehydes via benzoin condensation reactions) (Scheme 1). The resultant dithiolatonickel complexes were purified by column chromatography on silica gel using benzene or chloroform as eluent. Satisfactory elemental and TLC analyses data were obtained for all compounds and relevant data are given in Table 1.



[1a~g]

(i) KCN, (ii) P_2S_5, (iii) $NiCl_2 . 6H_2O$

Scheme 1

TABLE 1
Characterisation Data for Bis(1,2-diaryl-1,2-ethylenedithiolato)nickel Complexes

Compound			*Yield*[d] *(%)*	*Melting point* *(°C)*	*Found (%)*			*Calculated (%)*			λ_{max} *(nm)*[e]	$\varepsilon \times 10^{-4}$
No.	*R*	*R′*			*C*	*H*	*N*	*C*	*H*	*N*		
1a	C_6H_5	C_6H_5	52	294–295 dec.	62·07	3·62	—	61·88	3·71	—	860	3·17
1b	C_6H_5	p-$CH_3OC_6H_4$	24	252–253 dec.	60·17	3·92	—	59·70	4·01	—	885	3·18
1c	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	30	>300	58·87	4·18	—	57·92	4·25	—	>900	—
1d	p-$(CH_3)_2NC_6H_4$	C_6H_5	60	261–262 dec.	59·16	4·93	4·05	61·05	4·80	4·45	>900	—
1e	p-$(CH_3)_2NC_6H_4$	p-ClC_6H_4	52	281–283 dec.	55·24	4·32	4·10	55·02	4·04	4·01	>900	—
1f	p-$(CH_3)_2NC_6H_4$	o-ClC_6H_4	40	>300	55·71	4·06	4·40	55·02	4·04	4·01	>900	—
1g	p-$C_6H_5C_6H_4$	p-$C_6H_5C_6H_4$	38	>300	73·71	4·32	—	73·67	4·28	—	895	4·33
1h	C_6H_5	C_4H_3O[a]	4	>300	54·99	3·10	—	55·08	3·08	—	>900	—
1i	p-$(CH_3)_2NC_6H_4$	C_4H_3O	23	>300	53·22	5·48	4·30	55·18	4·30	4·60	>900	—
1j	C_4H_3O	C_4H_3O	4	>300	47·51	2·48	—	47·73	2·40	—	>900	—
1k	C_5H_4N[b]	C_5H_4N	6	>300	52·62	3·13	9·71	52·66	2·95	10·24	>900	—
1l	$C_{10}H_7$[c]	$C_{10}H_7$	7	>300	69·98	4·09	—	71·06	3·80	—	>900	—

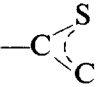
[a] 2-Furyl.

[b] 2-Pyridyl

[c] 1-Naphthyl.

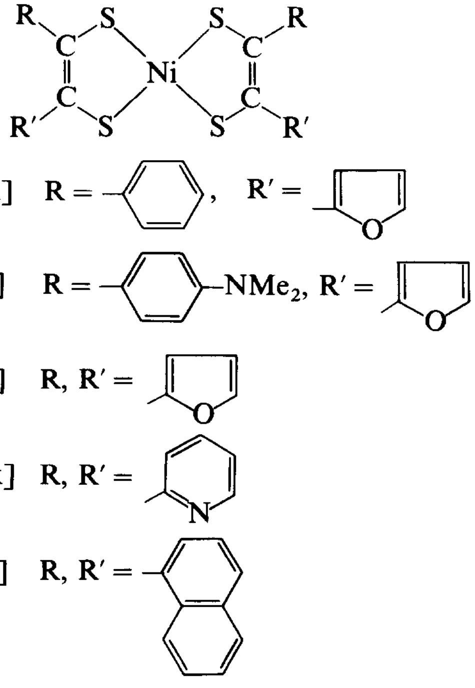
[d] The yields were based on the amounts of benzoin-type intermediates.

[e] In dichloromethane for **1a**–**1g** and in DMF for **1h**–**1l**.

Characteristic IR absorption bands for **1a** were observed at 1359 cm^{-1} (C=C stretching), 1136 and 882 cm^{-1} (R—C  $\mathrm{R{-}C}\genfrac{}{}{0pt}{}{\diagup \mathrm{S}}{\diagdown \mathrm{C}}$ system), 408 and 350 cm^{-1} (Ni—S).[7] The IR spectra of other complexes were similar to that of **1a**.

2.2 Preparation of dithiolatonickel complexes 1h–1l having condensed or heterocyclic rings

Little information is available on the preparation and nature of bis(1,2-ethylenedithiolato)nickel complexes having condensed or heterocyclic rings. In the present study, nickel complexes having naphthalene, pyridine or furan rings (**1j**–**1l**) were synthesised from α-naphthoin, pyridoin and furoin by the modified method described in the literature.[7] Asymmetrical nickel complexes **1h** and **1i**, having two pairs of phenyl and furan rings in the molecule, were also synthesised. In these reactions, the desired nickel complexes were obtained in lower yields, together with unknown products, in comparison with the reactions using symmetrical benzoin derivatives as starting materials. The complexes were purified by washing with methanol and acetone, and then by silica gel column chromatography. Yields and



Scheme 2

physical data are summarised in Table 1. Elemental and IR data were also satisfactory and supported the structure of **1h**–**1l**.

2.3 ESCA spectra of some nickel complexes

In order to elucidate further the structure of the complexes, ESCA analysis was carried out, and the spectra for **1a** and **1h** are shown in Fig. 1.

In Fig. 1, three main peaks based on S_{2p}, C_{1s} and Ni_{2p} were apparent for **1a**, and with **1h** an additional O_{1s} peak was observed. Binding energies of these elements are summarised in Table 2.

The binding energy of S_{2p} in **1h** was 163·90 eV, a value larger by *c*. 0·7 eV than in the case of **1a**. The peak (doublet) for C_{1s} in **1a** showed at 282·60 and 285·60 eV, and **1h** showed a single peak at 285·00 eV. The energy for Ni_{2p} in **1h** was 855·10 eV, a value smaller by *c*. 0·8 eV than that for **1a**. These differences between **1h** and **1a** suggest that there may be a slight difference in π-electron delocalisation in each five-membered ring, leading to a decrease in the photostabilising efficiency (as discussed in Section 2.4).

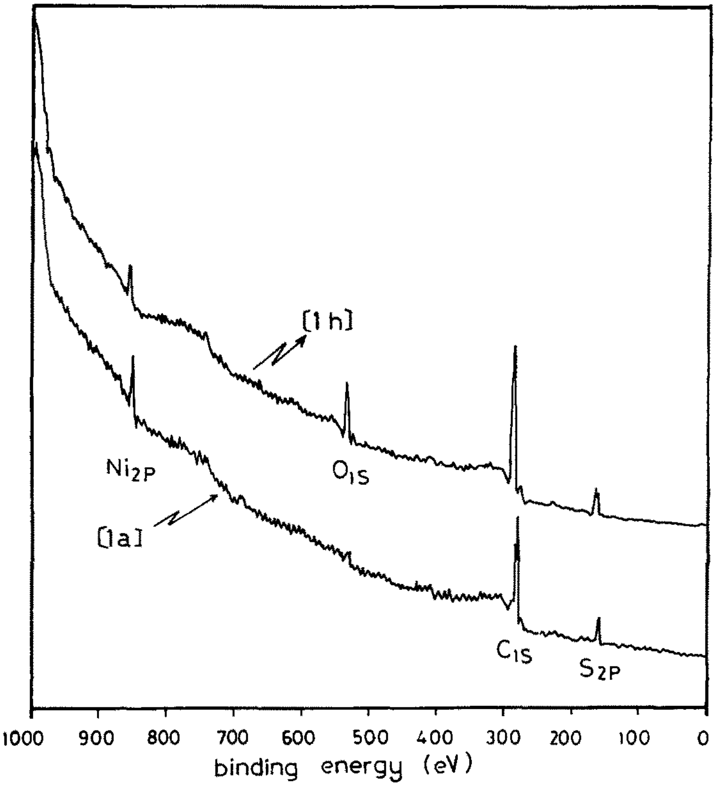


Fig. 1. Electron spectra (ESCA) of **1a** and **1h**. MgKα radiation, power 10 kV, 30 mA, 10^{-5} pa.

TABLE 2
Binding Energy for Some Complexes by ESCA Analysis[a]

Element	*Binding energy* (eV)	
	Complex **1a**	*Complex* **1h**
S_{2p}	163·20	163·90
C_{1s}	282·60, 285·60	285·00
O_{1s}	—	533·70
Ni_{2p}	855·90	855·10

[a] X-ray (magnesium Kα radiation), power 10 kV, 30 mA, 10^{-5} pa. Step energy, 0·10 eV; Sampling time, 200 ms; repeat time, 1.

2.4 Inhibiting effect on the photodegradation of dye

In order to investigate the effect of added complexes on the photostabilisation of organic dyes, cellulose acetate films containing the quinophthalone dye [2-(2-quinolyl)indan-1,3-dione, λ_{max} 418 and 442 nm] and various nickel complexes were prepared. The films were irradiated with filtered radiation (Toshiba coloured glass filter UV-39) using a 100 W high-pressure mercury lamp (Ushio-Electric Inc.) from a distance of 5 cm. After irradiation for 8 and 15 h, the relative percentage fading (conversion) of the dye was determined spectrophotometrically, and the results are shown in Table 3.

TABLE 3
Effect of the Dithiolatonickel Complexes on the Photostabilisation of Quinophthalone Dye in Cellulose Acetate Film[a]

Added complex	*Conversion (%)*[b]		*Added complex*	*Conversion (%)*[b]	
	8 h	*15 h*		*8 h*	*15 h*
None	18·2	38·6	**1g**	16·4	28·6
1a	4·6	5·5	**1h**	10·2	12·3
1b	5·0	7·7	**1i**	10·2	13·0
1c	4·3	10·6	**1j**	24·6	48·9
1d	4·7	6·3	**1k**	8·8	13·9
1e	4·3	9·1	**1l**	5·8	13·3
1f	13·3	18·9			

[a] In all runs the film was irradiated with a 100 W high-pressure mercury lamp (filtered light, $\lambda > 400$ nm); dye concentration $7{\cdot}0 \times 10^{-6}$ mol/g film, complex concentration $4{\cdot}7 \times 10^{-4}$ mol/g film.

[b] After 8 and 15 h of exposure to filtered radiation.

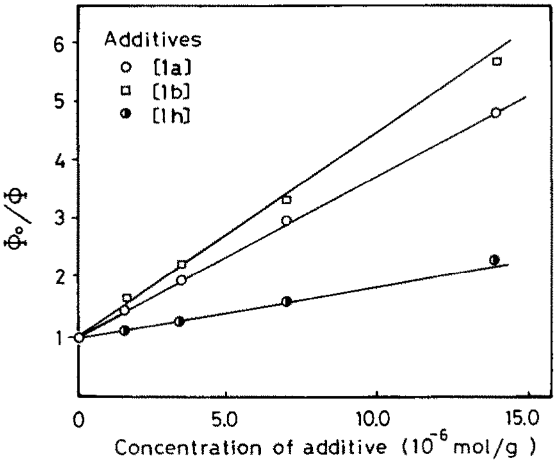


Fig. 2. Stern–Volmer plots for additives in the reaction inhibiting photodegradation of quinophthalone dye in cellulose acetate film; concentration of dye $7 \cdot 0 \times 10^{-6}$ mol/g film, irradiation with a 500 W high-pressure mercury lamp ($\lambda > 400$ nm).

From Table 3, it is apparent that the films containing these added nickel complexes (with the exception of the complex involving four furan rings in the symmetric ligand) had excellent lightfastness compared with the standard sample containing no additive. The effects with **1h**–**1i** and **1k**–**1l** having condensed or heterocyclic rings were small compared with those with **1a**–**1e**, which have phenyl or substituted phenyl rings. It is likely that the introduction of two or four furan rings in a ligand disadvantages the photostabilising effect.

The effect of the addition of some nickel complexes on the photostabilisation was investigated by Stern–Volmer analysis. The photodegradation quantum yield ratio, Φ_0/Φ, was plotted against the concentration of additives (Φ and Φ_0 are the quantum yields of the degradation reaction of quinophthalone in the presence and absence of the additive respectively). The results obtained for **1a**, **1b** and **1h** are shown in Fig. 2. The straight lines in the Stern–Volmer plots for **1a** and **1b** show that the addition of the complexes is effective in inhibiting the photo-oxidation of the dye by singlet oxygen.[8] The slope of the straight line for **1h** was relatively small. Similar tendencies were also observed in acetonitrile solution, with larger slopes than those in films.

2.5 Crystal structure of a dithiolatonickel complex

In connection with the photostabilising mechanism, an X-ray crystal structure of bis(dithiobenzil)nickel, **1a** (which could be obtained in a suitable single crystal), was analysed using a four-circle automatic diffractometer (Rigaku Electric Ltd) at room temperature. The structure was resolved by

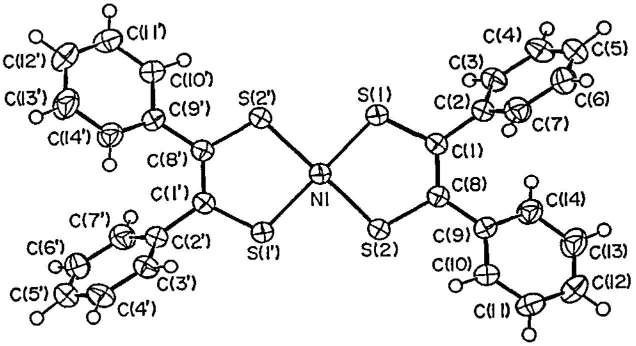
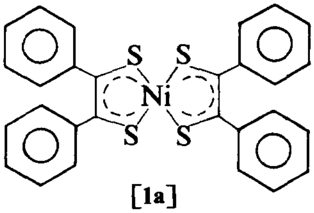


Fig. 3. The molecular structure of bis(dithiobenzil)nickel (**1a**) drawn by 50% probability thermal ellipsoids for non-hydrogen atoms, and by spheres of a fixed arbitrary radius for hydrogen atoms. Selected bond lengths (Å) are: Ni–S(1) 2·1220(4), Ni–S(2) 2·1195(6), S(1)–C(1) 1·698(1), S(2)–C(8) 1·712(2), C(1)–C(8) 1·396(2), C(1)–C(2) 1·485(2), C(8)–C(9) 1·482(2), C(9)–C(10) 1·399(2), C(10)–C(11) 1·387(3), C(9)–C(14) 1·396(2). Selected angles (°) are: S(1)–Ni–S(2) 91·00(2), S(2)–Ni–S(1') 89·00(2), Ni–S(1)–C(1) 105·76(5), Ni–S(2)–C(8) 106·2(1), S(1)–C(1)–C(2) 116·2(1), S(1)–C(1)–C(8) 119·4(1), C(2)–C(1)–C(8) 124·4(1), C(1)–C(2)–C(7) 119·7(1), S(2)–C(8)–C(1) 117·7(1), S(2)–C(8)–C(9) 116·8(1), C(1)–C(8)–C(9) 125·5(1), C(8)–C(9)–C(14) 122·0(1).

the heavy-atom method, and the numerical calculations were carried out on a computer. The resultant molecular structure is shown in Fig. 3.

The nickel atom must occupy the centre of symmetry. This structure is a planar arrangement,[9,10] except for parts of phenyl rings. Both phenyl groups (planes II and III) are planar and neither is conjugated with the five-membered chelating ring (plane I). The angle between planes I and II is 65·93(5)°, and 33·87(5)° between planes I and III. The angles between the two phenyl rings probably result from repulsion between the hydrogen atoms on C(7) and C(14). Bond lengths for the Ni–S(1) and Ni–S(2) bonds are 2·1220(4) Å and 2·1195(6) Å respectively. The S(1)–C(1) and S(2)–C(8) bond lengths are somewhat shorter than those usually observed in the S═C bond and the C(1)–C(8) distance is *c*. 0·06 Å longer than that normally found in the C═C bond. These observations suggest delocalisation of the π-electrons in the five-membered chelate ring, as shown in the molecular structure of **1a**.

A view of three adjacent molecules (A, B and C) is shown in Fig. 4, in which the molecules of A and B correlate with translation along the *a*-axis, and



[**1a**]

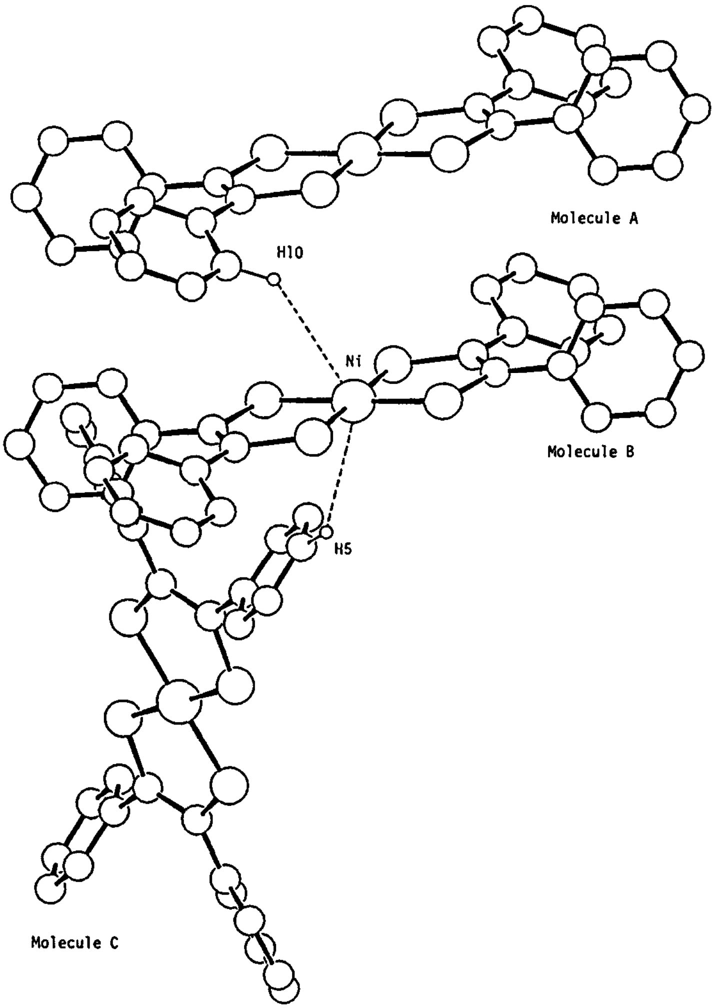


Fig. 4. Aspect of three adjacent molecules. Molecules A and B correlate with translation along the *a*-axis. Molecules B and C correlate with 2_1; distance (Å), Ni---H(5) 3·389, Ni---H(10) 3·296.

with a double helical twist towards the *b*-axis for molecules B and C. The shortest Ni---H contact was 3·296 Å, between a Ni atom in the molecular B and H(10) on the phenyl group in A along the *a*-axis. H(5) on C(5) in C along the *b*-axis makes a contact of 3·389 Å with the Ni atom. These distances are reasonably long. As seen in Fig. 4, there is an apparent absence of other atoms in the neighbourhood above and below the Ni atom.

This observation suggests that the Ni atom may be very capable of coordinating with oxygen atoms if singlet oxygen molecules are present in the neighbourhood, thus bringing about deactivation of singlet oxygen by interaction involving energy transfer[11-14] and/or charge transfer mechanisms.[11] However, further experiments are necessary to study the detailed mechanisms pertinent to the quenching reaction.

3 EXPERIMENTAL

Visible and IR spectra were measured using Shimadzu UV-250 and IR-420 spectrophotometers respectively. Elemental analyses were recorded on a Yanaco CHN recorder MT-2. ESCA analyses were measured using a Shimadzu ESCA-850 operating at 10 kV, 30 mA.

3.1 Starting materials for the synthesis of the complexes

Benzoin and anisoin were purchased from Tokyo Chemical Industry Co. Ltd. Furoin and α-pyridoin were purchased from Aldrich, and were used without further purification. 4-Dimethylaminobenzoin, 2′ (or 4′)-chloro-4-dimethylaminobenzoin, 4-dimethylaminobenzofuroin, 4,4′-diphenylbenzoin and α-naphthoin were synthesised from the corresponding aromatic aldehydes according to the literature method.[15]

3.2 General procedure for the synthesis of dithiolato nickel complexes

Nickel complexes (**1a**, **1c** and **1g**) with symmetrical phenyl rings were prepared from benzoin or its derivatives by Schrauzer & Mayweg's method.[7] Complexes **1b**, **1d** and **1e**–**1f** having asymmetrical substituted phenyl rings were obtained from a mixture of two different benzoin derivatives by the same procedure. The products were purified by column chromatography on silica gel using benzene or chloroform as eluent.

3.3 Syntheses of nickel complexes (1h–1l) having condensed or heterocyclic rings

A mixture of α-pyridoin (2·1 g; 0·01 mol) and phosphorus pentasulphide (3·2 g) in 120 ml of dioxane was vigorously stirred for 3 h under nitrogen. After cooling to room temperature, the reaction liquor was filtered and added to DMF (120 ml). To the DMF solution, a solution of $NiCl.6H_2O$ (1·2 g) in water (17 ml) was added dropwise, and the mixture was then stirred for 2 h at 70–80°C. The filtered solid was washed several times with water, methanol and acetone, and 0·7 g of **1k** was obtained as dark brown crystals.

α-Naphthoin (2·0 g) was refluxed with 3·0 g of P_2S_5 in 60 ml of dioxane for 3 h (hydrogen sulphide evolved). The reaction mixture was cooled and filtered. To the filtrate, 15 ml of an aqueous solution containing $NiCl_2 . 6H_2O$ (3·0 g) was added, and after stirring for 2 h, the mixture was cooled, filtered, washed, and dried. The crude material was purified by column chromatography on silica gel using benzene–acetone (4:1), and the eluted liquor was evaporated under reduced pressure to give **1l** (yield 6·5%, dark green crystals).

3.4 Photodegradation of quinophthalone dye and Stern–Volmer plots

A solution (15 ml) of DMF–acetone (1:1, v/v) containing 1·5 g of cellulose acetate powder, $1{\cdot}05 \times 10^{-5}$ mol of the quinophthalone dye and $7{\cdot}0 \times 10^{-4}$ mol of the nickel complex were applied to a glass plate using a film applicator and dried in a vacuum desiccator for 20 h. The polymer film was removed from the plate and dried at $40 \pm 2°C$ under vacuum for another 5 h. The films (thickness, 40 μm) were exposed in air to the radiation from a 100 W high-pressure mercury lamp filtered through a 10% sodium nitrite filter solution, the lamp being placed about 5 cm from the film. The conversion (%) was determined photometrically.

For the Stern–Volmer experiments, quantum yields of the photodegradation in cellulose acetate films or air-saturated acetonitrile solution ($1{\cdot}0 \times 10^{-4}$ M) were determined in a similar manner to that previously described.[16]

3.5 Crystal structure determination of 1a

Crystals grown from a dichloromethane solution were dark green. The cell dimensions were obtained from zero-layer Weissenberg photographs (CuKα, $\lambda = 1{\cdot}5418$ Å), and the diffraction intensities were measured on a Rigaku four-circle diffractometer using graphite-monochromated MoKα ($\lambda = 0{\cdot}710\,69$ Å) radiation at room temperature. Intensity data were measured using the ω–2θ scan technique (4° min^{-1}); 3196 independent reflections with values up to 60° ($|F_0| > 3\sigma(|F_0|)$) were used for the analysis. Lorentz and polarization corrections were made as usual, but absorption correction was omitted.

Crystal data: $C_{28}H_{20}S_4Ni$; $M = 543{\cdot}42$; monoclinic; space group $p2_1/n$; $a = 5{\cdot}937(1)$, $b = 11{\cdot}092(2)$, $c = 18{\cdot}621(2)$ Å, $\beta = 92{\cdot}421(1)°$, $U = 1225{\cdot}2(4)$ Å^3; $Z = 2$; $D_m = 1{\cdot}419$ g cm^{-3}, $D_x = 1{\cdot}473$ g cm^{-3}; μ (MoKα) $= 11{\cdot}33$ cm^{-1}; crystal size 0·74 mm × 0·47 mm × 0·43 mm.

In a unit cell, there are two molecules so that nickel atoms must occupy the centre of symmetry and are co-ordinated by four sulphur atoms. The sulphur atoms were located in a three-dimensional Patterson synthesis. The refinement was performed by the block-diagonal least-squares method. An R value $\Sigma(||F_0| - |F_c||)/\Sigma|F_0|$ and an R_w value $[\Sigma_w(|F_0| - |F_c|)^2/\Sigma_w|F_0|^2]^{1/2}$ of 0·360 and 0·424 respectively were obtained. A three-dimensional difference Fourier synthesis was computed and peaks corresponding to 14 carbon atoms were identified. Isotropic refinement including these atoms reduced R to 0·117 ($R_w = 0{\cdot}110$). Anisotropic refinement of all non-hydrogen atoms was carried out ($R = 0{\cdot}041$, $R_w = 0{\cdot}071$). A difference synthesis was then computed and peaks for hydrogen atoms were found in the expected positions. These atoms were added with isotropic vibration parameters and the final refinements were carried out to give the R value of 0·029 and the R_w value of 0·046. All the computations were carried out on a FACOM 270-20 computer in Kawnseigakuin University.

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