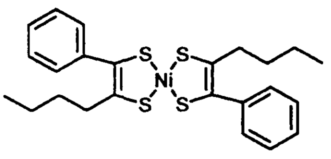
Preparation, Properties and Crystal Structures of New Nickel(II) Complexes of 1,2-Asymmetrically Substituted Dithiolenes for Third-order Non-linear Optical Applications†

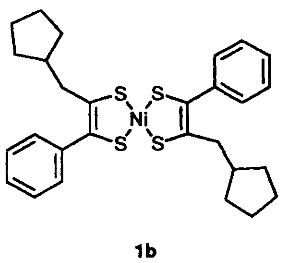
Callum A. S. Hill,[a] **Adam Charlton,**[a] **Allan E. Underhill,***[,a] **K. M. Abdul Malik,**[b] **Michael B. Hursthouse,**[b] **A. I. Karaulov,**[b] **Steven N. Oliver**[c] **and Steven V. Kershaw**[c]
[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK*
[b] *Department of Chemistry, University of Wales, Cardiff CF1 3TB, UK*
[c] *British Telecom Research Limited, Martlesham Heath, Ipswich, Suffolk IP5 7RE, UK*

Three new nickel(II) complexes of 1-alkyl-2-phenyl asymmetrically substituted dithiolenes $[\mathrm{Ni(SCR^1{=}CR^2S)_2}]$ (R^1 = Ph; R^2 = Bu^n, cyclopentylmethyl or 4-pentylcyclohexyl) have been prepared and their electrochemical properties and near-IR spectra studied. The crystal structures of the complexes in which R^2 = Bu^n or cyclopentylmethyl have been determined. The presence of bulky substituents adjacent to the ring has no affect upon the electrochemical or near-infrared properties. Third-order non-linear optical coefficients were measured by degenerate four-wave mixing.

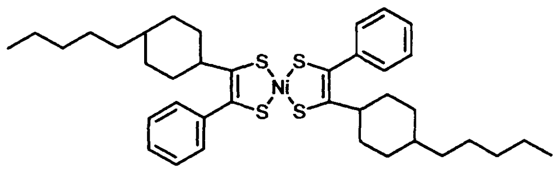
Since their initial synthesis in the 1930s a large number of metal bis(dithiolenes) have been reported.[1,2] Interest in these materials has increased over the past decade since they exhibit many unusual optical,[3] electronic[4] and electrochemical[5] properties. They exhibit strong absorption bands in the near-infrared region of the electromagnetic spectrum and by choice of suitable substituents it is possible to tune the absorption maximum from 700 to 1440 nm. They are also known to be very stable to intense irradiation in this region and for example have been used as Q-switch dyes for Nd-YAG lasers operating at 1064 nm.[3] For the above reasons we have been investigating the possibility of using resonance enhancement in metal bis(dithiolenes) to increase the value of the third-order non-linearity ($\chi^{(3)}$).[6,7] Extensive investigations of a variety of metal dithiolenes have shown that it is indeed possible to observe resonance enhancement of the value of $\chi^{(3)}$ but that this occurs at the expense of an increase in the linear absorption coefficient (α).[8] When the effect of the linear absorption coefficient is taken into account it is found that a trade-off in these two values ($\chi^{(3)}$ *vs.* α) occurs at a critical detuning from the laser fundamental of 1064 nm with materials absorbing in the region of 800–810 nm exhibiting the largest values of $\chi^{(3)}/\alpha$.[9] Studies of nickel dithiolenes as guests in poly(methyl methacrylate) (pmma) hosts have shown similar properties,[7] but in this case the additional problem of material compatibility with the polymer host is also of importance. When all these matters are addressed the best material is found to be the compound bis[1-butyl-2-phenylethene-1,2-dithiolato(2−)-*S*,*S*′]-nickel(II) **1a**. This material exhibits the optimum properties of an absorption band maximum at 800 nm coupled with good solubility and compatibility with the polymer.[10] To improve upon these latter properties we have embarked upon a programme to synthesise complexes of other nickel dithiolenes having the 1-alkyl-2-phenyl asymmetric substitution pattern. In particular, we wished to investigate the possible effects of phenyl ring rotation upon the electronic spectrum and the non-linearity of the complexes. A theoretical study by Kodaka *et al.*[11] on the structurally related compound 2-[cyano(methoxycarbonyl)methylene]-4-phenyl-1,3-dithiole has shown that the magnitude of the second-order hyperpolarisability β_x is strongly dependent upon the dihedral angle between the phenyl ring and dithiole group. The extent to which this would change the third-order properties was not clear, but we reasoned that the addition of bulky groups adjacent to the phenyl ring would affect the ability of the ring to rotate and limit the conjugation between the ring and the dithiolene core. It was also considered that if phenyl ring libration could be limited by the presence of the bulky alkyl groups, then this might result in a decrease in the width of the absorption band and thus lead to an enhancement of the figure of merit $\chi^{(3)}/\alpha$. Furthermore we found that metal complexes of the 1-butyl-2-phenyl dithiolenes exhibited a tendency to crystallise in pmma polymer matrices at concentra-



1a



1b



1c

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

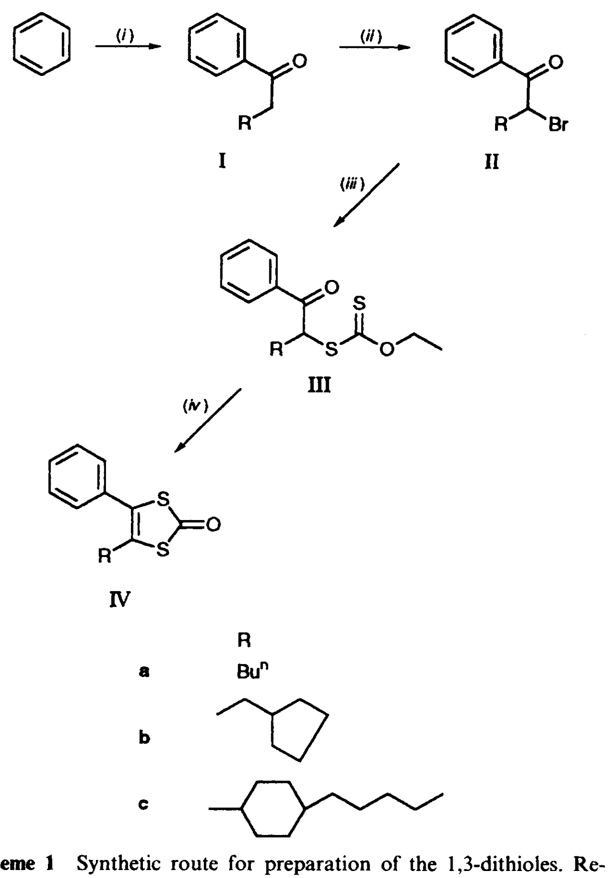
tions above 20% w/w leading to a fall in device-related figures of merit.[10] It was thought that suitable bulky substituents might decrease the tendency to aggregate, allowing higher loadings in the polymer film. We now report the syntheses of three new nickel(II) complexes of 1-alkyl-2-phenyl asymmetrically substituted dithiolenes together with their electronic third-order non-linear optical and electrochemical properties and crystal structures of two of the complexes.

Results and Discussion

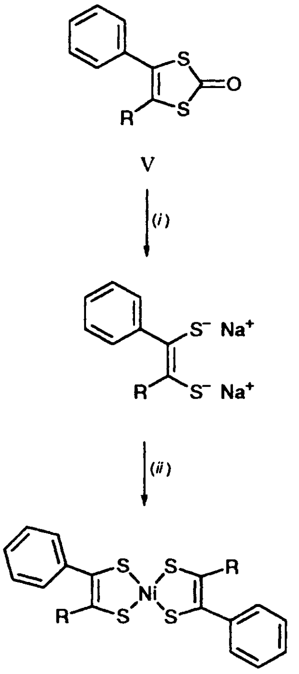
Preparation.—The synthesis of the 1,3-dithioles was based upon the method first reported by Mueller-Westerhoff *et al.*[12] for metal bis(dithiolene) nematic liquid crystals. The procedure is given in Scheme 1. It involves the Friedel–Crafts acylation of a suitable acid chloride or acid bromide with benzene. If necessary, the product of this reaction was brominated to yield an α-bromo ketone. Reaction of the latter with potassium *O*-ethyl dithiocarbonate yielded the xanthate ester which was treated with concentrated H_2SO_4 to give the substituted 1,3-dithiol-2-one derivatives. To obtain a pure product it was found necessary to recrystallise the $K[S_2COEt]$ from acetone–diethyl ether before use. The ring-closure reaction using concentrated H_2SO_4 was found to produce various unidentified side products which were removed by column chromatography on silica. Ring-closure reactions were also performed using 48% HBr–acetic acid (1 : 1) but this procedure yielded products of inferior purity.

The formation of the metal complexes is shown in Scheme 2. The disodium salt of the ethenedithiolate was prepared using NaOMe–MeOH or NaOEt–EtOH and an alcoholic solution of tetra-*n*-butylammonium bromide or tetraethylammonium bromide (1 equivalent based on the dithiolate) was added. To this solution was added dropwise a solution of nickel(II) chloride hexahydrate. Formation of the dianionic nickel complex was accompanied by a colour change from yellow to red-brown. It is essential to add the nickel salt slowly to prevent the formation of the insoluble $Ni[Ni(dithiolene)_2]$ salt. The tetraalkylammonium salt was isolated as a red-brown solid, which was dissolved in acetone and filtered. Addition of 2 equivalents of iodine yielded the neutral nickel complex which was purified by recrystallisation from dichloromethane–methanol All the nickel complexes gave satisfactory elemental analyses when purified.

Optical and Electrochemical Properties.—All the neutral complexes exhibited an intense near-infrared absorption band at approximately 800 nm characteristic of nicikel bis(dithiolenes) (Table 1). This intense absorption has been assigned to a $2B_{1u} \longrightarrow 3B_{2g}$ transition (D_{2h}),[13] an allowed *x*-polarised transition. It has been calculated[13] that the $2B_{1u}$ and $3B_{2g}$ states have 0 and 16% contribution from the metal respectively. The position of the band associated with this transition would therefore be expected to be sensitive to variations of substituents on the ligand. Determination of full-width half-maximum (f.w.h.m.) values for the metal complexes shows that the varying steric bulk of the group adjacent to the phenyl ring substituent has no effect upon the 'width' of the absorption band. It might have been expected that a bulky group would limit the ability of the phenyl ring to rotate and alter the extent of conjugation between the phenyl ring and the ditholene core, causing a variation in the energy of the HOMO (highest occupied) and LUMO (lowest unoccupied molecular orbital) and thus resulting in a change in λ_{max} and the width of the absorption band. The absence of this effect indicates that either there is little difference between the steric effect of the *n*-butyl and cyclohexyl groups or that the absorption band is not sensitive to such subtle effects. Measurement of the absorption coefficients of the three complexes shows a small increase in ε_{max} values as the steric bulk of the group increases (Table 1). This increase may be the result of a small narrowing of the band or may be due to an increase in oscillator strength of the transition.



Scheme 1 Synthetic route for preparation of the 1,3-dithioles. Reagents and conditions: (*i*) RCH_2COCl–$AlCl_3$, CH_2Cl_2, 18 h; (*ii*) Br_2–CH_2Cl_2, room temperature (r.t.); (*iii*) $K[S_2COEt]$, Me_2CO, r.t.; (*iv*) concentrated H_2SO_4, 0 °C



1

Scheme 2 Preparation of metal complexes. Reagents and conditions: (*i*) NaOEt–EtOH; (*ii*) NR_4Br, $NiCl_2{\cdot}6H_2O$ then iodine

Electrochemical studies have shown that all the three complexes exhibit two quasi-reversible redox processes at

Table 1 Electronic absorption data, electrochemical properties and third-order non-linear optical properties

	1a	**1b**	**1c**	$[Ni(S_2C_2Ph_2)_2]$
$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$	21 333	24 800	28 380	—
λ_{max}/nm	800	800	800	—
$E_{\frac{1}{2}}([ML_2]^{2-} \rightleftharpoons [ML_2]^-)$*/V	−1.42	−1.43	−1.44	−1.27
$E_{\frac{1}{2}}([ML_2]^- \rightleftharpoons [ML_2])$*/V	0.60	−0.60	−0.61	−0.47
α/cm^{-1}	0.14	0.15	0.13	—
$10^{20}\ \chi^{(3)}{}_{1111}/m^2\ V^{-2}$	1.3	1.1	2.0	—
$10^{11}\ n_2/cm^2\ kW^{-1}$	2.4	2.1	3.8	—
W	4.8	4.0	8.5	

* Relative to ferrocene.

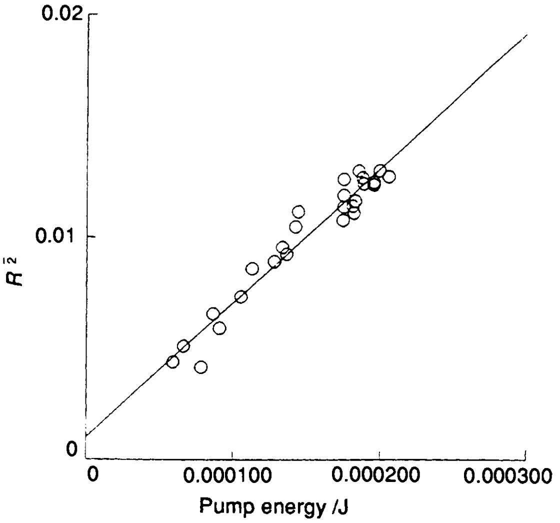


Fig. 1 Phase-conjugate reflectivity plot for complex **1b**

ca. −1.43 and at *ca.* −0.60 V relative to the ferrocene–ferrocenium couple. These two processes are typical of nickel dithiolenes and are assigned to the dianion $\rightleftharpoons$ monoanion and monoanion $\rightleftharpoons$ neutral redox processes respectively, *i.e.* $[ML_2]^{2-} \rightleftharpoons [ML_2]^- \rightleftharpoons [ML_2]$.[14] As with the electronic spectra, the steric effect of the group adjacent to the phenyl ring does not exert any appreciable influence upon the electrochemical properties of the three complexes. There is a slight negative shift of the voltages for the two redox processes compared with the tetraphenyl-substituted nickel bis(dithiolene) (Table 1). This small shift is in agreement with results obtained by Olson *et al.*[15] in a study of a large number of metal bis(dithiolenes) including the asymmetrically substituted bis[1-methyl-2-phenylethene-1,2-dithiolato(2−)-*S*,*S*′]nickel(II). It is presumably due to the electron-donating effect of the alkyl group into the dithiolene core.

Non-linear Optical Studies.—Results from the degenerate four-wave mixing measurements are presented in Table 1, together with measurements of the linear absorption coefficient (α) at 1064 nm. All values are normalised to a concentration of 10^{18} molecules cm^{-3} (1.6×10^{-3} mol dm^{-3}) A typical phase-conjugate reflectivity plot for complex **1b** is shown in Fig. 1. The best fit (linear regression) drawn through the data points is a straight line passing close to the origin, there being no evidence of saturation from this plot. A plot of $\log_{10}$ (phase-conjugate reflectivity) *vs.* $\log_{10}$ (input power) for these data points gives a slope of 2.85, acceptably close to the value of 3 required for a third-order process. It has been found that samples absorbing above 810 nm do exhibit saturation and it is necessary to adjust the concentration of the solution to avoid interference from these effects.[10] All compounds in the series have comparable third-order responses, the variation between samples being within the experimental error encountered with this technique. In view of the similar structures of these materials it is not surprising that such a result should be obtained. Similarly, the values of α are all comparable, showing that the bulkiness of the alkyl substituent has little effect upon the absorption band profile. The data include a calculation of the Stegeman figure of merit (W), equation (1), where Δn_{sat} is the largest observable

$$W = \Delta n_{sat}/\alpha\lambda \qquad (1)$$

change in refractive index before saturation, α is the linear absorption coefficient and λ is the measurement wavelength. We calculated this value from equation (2) where I is the

$$W = n_2 I/\alpha\lambda \qquad (2)$$

maximum pump beam intensity before sample damage occurs (2GW cm^{-2} in thin films), n_2 is the non-linear refractive index, α and λ have the same meaning as in equation (1).

For a waveguide device such as a Mach–Zehnder interferometer or a directional coupler to show switching at reasonable power levels, $W > \pi/2$ is required.[6] All samples of this series exhibited W values greater than the minimum suggesting that they are suitable for device use.

The question arises as to whether the large observed non-linearity is thermal or electronic in origin. We believe that the dominant non-linear process in materials absorbing at 800 nm can be attributed to an electronic origin, based on the following observations:[6,9,10,16] (1) a ratio close to 3:1 is observed for $\chi^{(3)}{}_{1111}/\chi^{(3)}{}_{1221}$ where $\chi^{(3)}{}_{1111}$ represents the value obtained when the probe and pulse beams are parallel polarised and $\chi^{(3)}{}_{1221}$ when the probe and pulse are orthogonally polarised; this is what would be expected for an electronic non-absorptive origin of $\chi^{(3)}$; (2) comparison of z-scan and DFWM (degenerate four-wave mixing) experiments shows a very close correspondence between coefficients; (3) results obtained in solution and the solid state show a close correspondence, which would not be the case if thermal effects dominated since the molecular rotation or migration times would be very different in the two media; (4) time-delay studies have shown that, in the case of complex **1a**, 80% of the signal decays within the laser pulse width[17] (100 ps); a thermal mechanism would exhibit decay times of the order of nanoseconds.

These observations, coupled with preliminary z-scan measurements at 1.3 μm which show that in the case of complex **1a** a substantial percentage of the non-linearity remains at this wavelength, all indicate that a non-thermal origin of $\chi^{(3)}$ is most likely. Having previously established the potential of **1a**, we were concerned with trying to improve upon the performance of this material. By introducing bulky groups adjacent to the phenyl ring we hoped to see an improvement in the figure of merit W, by reducing the width of the near-infrared absorption band, leading to a concomitant reduction in the linear absorption coefficient (α). Unfortunately, we have observed no such effect, the increase in W observed with complex **1c** being due to the larger value of n_2 compared to that with **1a**. It is likely that this is purely an artifact of the experiment and no

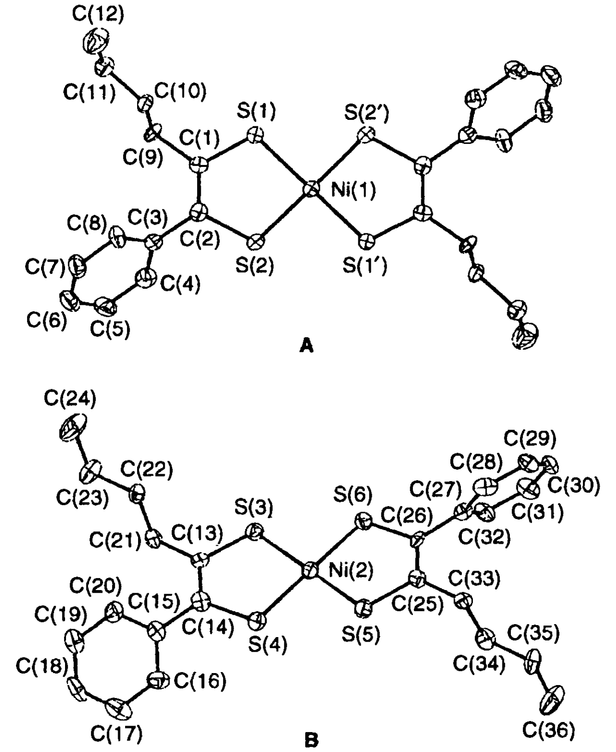


Fig. 2 Crystallographic structure of complex **1a**, showing the two forms mentioned in the text

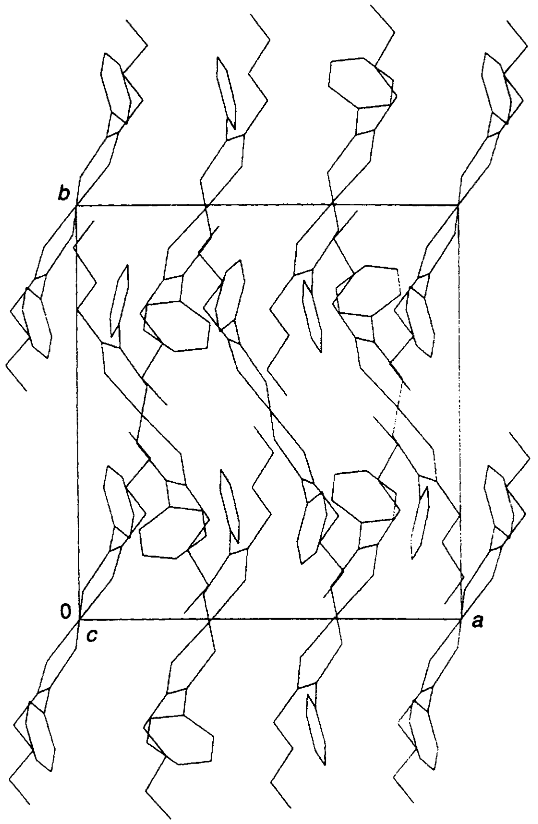


Fig. 3 Crystal packing in the unit cell of complex **1a**

significance can be attached to this result. It was also postulated that bulky groups would delay the onset of aggregation in polymeric matrices such as poly(methyl methacrylate). Complex **1b** shows lower compatibility with pmma than does **1a**, presumably because the cyclopentyl ring is more rigid than the linear *n*-butyl group. Insufficient quantities of **1c** were obtained to study the compatibility of this system with pmma in detail.

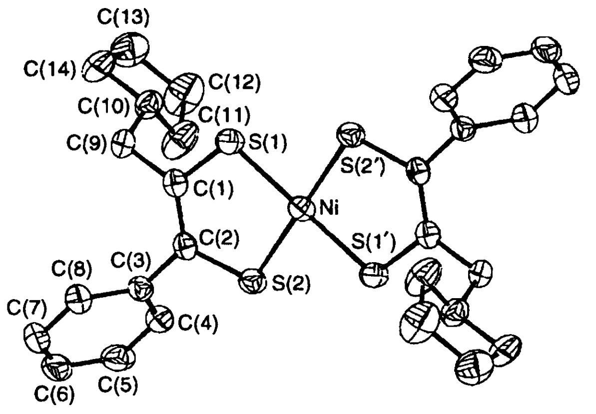


Fig. 4 Crystallographic structure of complex **1b**

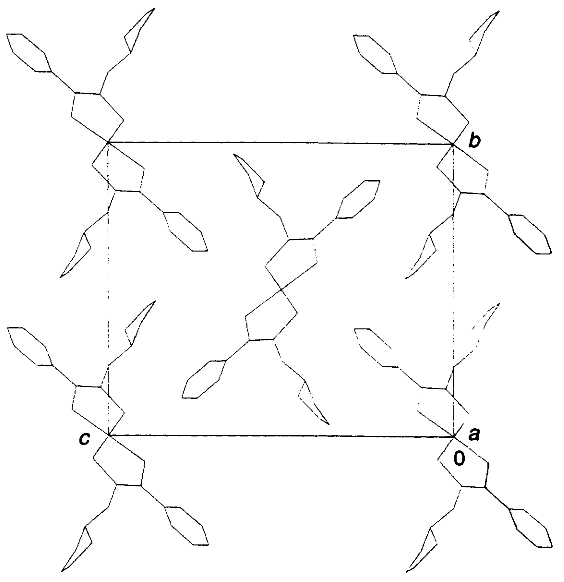


Fig. 5 Packing in the unit cell of complex **1b**

X-Ray Structural Studies.—The molecular structures of complexes **1a** and **1b** are shown in Figs. 2 and 4 respectively; the unit-cell packings are shown in Figs. 3 (**1a**) and 5 (**1b**). Selected bond lengths and angles for the two complexes are presented in Table 2. Both have a square-planar *trans* configuration which has been observed before in solid-state studies of asymmetrically substituted dithiolenes.[18] Complex **1a** forms approximately columnar molecular stacks along *a* with some degree of disorder within the stacks. The molecules are parallel to one another within the stacks, with Ni(1)$\cdots$Ni(2) and Ni(2)$\cdots$Ni(2) (at $1 - x, -y, -z$) distances of 4.562 and 4.596 Å respectively. The intermolecular S$\cdots$S distances, 3.97–4.74 Å, are all greater than the sum of the van der Waals radii for sulfur (3.60 Å). There are three unique non-bonded short contacts involving the Ni and S atoms in the neighbouring molecules, 3.684 [Ni(1)$\cdots$S(5)], 3.936 [Ni(2)$\cdots$S(2)] and 3.715 Å [Ni(2)$\cdots$S(3) (at $1 - x, -y, -z$)].

An interesting feature of the structure of complex **1a** is the presence of two independent molecules, **A** and **B** in Fig. 2, with **A** having a crystallographic centre of symmetry but **B** without any symmetry. Although the corresponding bond lengths and angles in the two molecules are virtually identical, the phenyl rings on the two dithiolene moieties in **B** are oriented differently with respect to the nickel dithiolene core. Thus the dihedral

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1a** and **1b**

	1a		
	Molecule A	Molecule B	**1b**
Ni(1)–S(1)	2.111(2)		2.118(1)
Ni(1)–S(2)	2.122(2)		2.121(1)
Ni(2)–S(3)		2.116(2)	
Ni(2)–S(4)		2.115(2)	
Ni(2)–S(5)		2.119(2)	
Ni(2)–S(6)		2.125(2)	
S(1)–C(1)	1.706(7)		1.701(2)
S(2)–C(2)	1.731(7)		1.712(2)
S(3)–C(13)		1.699(7)	
S(4)–C(14)		1.704(7)	
S(5)–C(25)		1.705(7)	
S(6)–C(26)		1.702(7)	
C(1)–C(2)	1.353(7)		1.373(3)
C(13)–C(14)		1.375(7)	
C(25)–C(26)		1.368(7)	
S(1)–Ni(1)–S(2)	91.22(7)		91.26(3)
S(1)–Ni(1)–S(2′)*	88.78(7)		88.74(3)
S(3)–Ni(2)–S(4)		91.07(9)	
S(5)–Ni(2)–S(6)		91.43(9)	
S(3)–Ni(2)–S(6)		89.50(8)	
S(4)–Ni(2)–S(5)		88.01(8)	
S(3)–Ni(2)–S(5)		177.40(10)	
S(4)–Ni(2)–S(6)		179.43(10)	
Ni(1)–S(1)–C(1)	105.8(2)		105.67(8)
Ni(1)–S(2)–C(2)	104.8(2)		104.97(8)
Ni(2)–S(3)–C(13)		105.4(2)	
Ni(2)–S(4)–C(14)		105.6(2)	
Ni(2)–S(5)–C(25)		105.1(2)	
Ni(2)–S(6)–C(26)		104.8(2)	
S(1)–C(1)–C(2)	119.3(6)		118.7(2)
S(2)–C(2)–C(1)	118.9(5)		119.4(2)
S(3)–C(13)–C(14)		119.3(5)	
S(4)–C(14)–C(13)		118.5(5)	
S(5)–C(25)–C(26)		119.1(5)	
S(6)–C(26)–C(25)		119.6(5)	

* The primed atom is related to the unprimed one by a centre of symmetry.

angles between the NiS$_2$C$_2$ planes and the phenyl rings at each end of the asymmetric molecules are 111.8 and 127.4°, which are probably determined by packing requirements. The corresponding dihedral angles in the centrosymmetric molecules are both identical (117.5°). The C=C bond lengths are 1.353(7) in **A** and 1.368(7) and 1.375(7) Å in **B**. The average Ni–S and S–C distances are 2.116 and 1.708 respectively.

In complex **1b** (Fig. 4) the molecules have a centre of symmetry, the dihedral angle between the nickel–sulfur core and the phenyl rings being 117.5°. The average intramolecular Ni–S, S–C and C=C bond distances are 2.120, 1.706 and 1.373 Å respectively, which are very similar to the corresponding values in **1a**. There are no intermolecular S–S contacts less than 3.75 Å. The X-ray data do not provide conclusive evidence that the presence of the cyclopentylmethyl group has any effect upon the dihedral angle between the phenyl ring and the nickel–dithiolene core. It is likely that crystal-packing effects are the dominant processes here. There is no evidence for substantial intermolecular interactions in the solid state.

It has been observed that in guest–host systems of molecule **1a** in pmma there is a dramatic increase in two-photon absorption when the guest concentration exceeds 10^{20} molecules cm^{-3}.[10] Molecular aggregation was considered to be the most likely explanation for this effect, with the possibility of a two-photon allowed transition between molecules taking place. In view of the large intermolecular distances involved this would seem a less attractive hypothesis. A more likely explanation would be a change in the symmetry of the system in an aggregated structure compared to isolated molecules.

Conclusion

The synthesis, characterisation and non-linear optical properties of a series of asymmetrically substituted nickel bis(dithiolene) complexes have been described. The introduction of sterically bulky groups adjacent to the phenyl ring has no effect on either the position of the absorption maximum nor the profile of the near-infrared spectrum. Consequently, the linear absorption coefficient (α) in these materials is unchanged and solution DFWM studies indicate no further improvement on the device-orientated *W* figure of merit.

Further work is required concerning the improvement in the compatibility of these monomeric materials with pmma, for use in guest/host DFWM studies.

Experimental

Near-infrared spectra were recorded on a Perkin-Elmer λ9 spectrophotometer with dichloromethane solutions, infrared spectra as thin films sandwiched between NaCl plates using a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyser, using trifluoroacetanilide as reference material. Proton NMR spectra were recorded on CDCl$_3$ solutions using a Bruker AC-250 250 MHz spectrometer using SiMe$_4$ as internal standard and are reported in ppm on the δ scale. Mass spectra were run on a Finnigan Mat 1020 spectrometer, using the solid-probe facility and in the electron impact (EI) mode. Cyclic voltammetry was performed using an EG&G Princeton Applied Research model 264A polarographic analyser, with software data processing. Experiments were conducted using dry, freshly distilled dichloromethane as solvent with 0.1 mol dm^{-3} [NBu$^n{}_4$][BF$_4$] as supporting electrolyte. A platinum-button working electrode and platinum-spade auxiliary electrode were used in conjugation with either silver wire or an Ag–AgCl electrode as reference. A ferrocene standard was run before and after cyclic voltammetry experiments and all $E_{\frac{1}{2}}$ values are quoted relative to that of the ferrocene–ferrocenium couple.

(4-Pentylcyclohexyl)ethanoic acid was a gift from Merck, Pool. All other starting materials were obtained from Aldrich and used without further purification except for potassium *O*-ethyl dithiocarbonate which was recrystallised prior to use. Ethanol or methanol used in the preparation of the metal complexes was dried by distillation over magnesium and degassed before use. Metal complexes were prepared under a dry argon blanket.

Non-linear optical measurements were made at 1064 nm for the dithiolenes in dichloromethane solution by degenerate four-wave mixing using a retroreflecting pump geometry. Two intense pump beams were formed from a single mode-locked pulse (pulse width 100 ps) selected from the Q-switch envelope of a Nd:YAG laser and its retroreflected image from a plane dielectric mirror placed immediately behind the sample which was contained in a 2 mm path length cuvette. A weak (10% of pump) probe beam was split off the forward pump which then interacted with the grating set up between the two pump beams. For the experiments reported an all-parallel polarised beam set-up was used ($\chi^{(3)}{}_{1111}$). The phase conjugate (p.c.) beam, retro-reflected along the path of the forward probe beam, was split off and detected. The square root of the reflectivity $R\,(= E_{pc}/E_{pump})$ was plotted against input pump energy and the slope, *G*, of the plot ratioed to that of a reference CS$_2$ sample for which we take $\chi^{(3)}$ as 2.5×10^{-20} m^2 V^{-2} (equivalent to an n_2 of 3.6×10^{-11} cm^2 kW^{-1}.[19,20] From this can be derived the $\chi^{(3)}$ and hence n_2 of the solution.[21] Full experimental details have been given elsewhere.[6]

X-Ray Crystallography.—Crystals of complexes **1a** and **1b** suitable for X-ray work were grown by slow evaporation of dichloromethane solutions. All measurements were made at 150 K using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator using Mo-Kα radiation (λ = 0.710 69 Å) by following previously described procedures.[22] The structures were solved by direct methods (SHELXS)[23] and refined by full-matrix least squares (SHELXL 93)[24] using all unique F_o^2 data corrected for Lorentz and polarisation factors, and absorption effects (DIFABS).[25] In all cases the non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included in idealised positions with the U_{iso} values set at 1.2 U_{eq} of the parent carbons. Sources of scattering factors were as in ref. 24. The calculations were done on a 486DS2/66 personal computer. Crystal data and details of data collection and structure refinement are presented in Table 3 and the fractional coordinates of the non-hydrogen atoms are given in Tables 4 (complex **1a**) and 5 (**1b**).

Table 3 Crystal data and details of data collection and structure refinement for complexes **1a** and **1b**[a]

	1a	**1b**
Formula	$C_{24}H_{28}NiS_4$	$C_{28}H_{32}NiS_4$
M	503.41	555.49
a/Å	13.724(5)	5.9528(3)
b/Å	14.956(3)	13.899(2)
c/Å	17.609(4)	16.268(2)
β/°	93.23(2)	92.82(1)
U/Å^3	3609(2)	1344.3(3)
Z	6	2
D_c/g cm^{-3}	1.390	1.372
F(000)	1584	584
μ/cm^{-1}	11.62	10.47
Crystal size/mm	0.25 × 0.12 × 0.06	0.35 × 0.15 × 0.08
θ range for data/°	1.79–25.12	2.51–29.42
hkl ranges	−15 to 12, −10 to 17, −20 to 19	−7 to 5, −19 to 12, −19 to 21
Total data measured	7602	7523
Total unique (R_{int})	4578 (0.073)	3129 (0.037)
Absorption correction factors, minimum, maximum	0.877, 1.200	0.866, 1.103
No. of parameters/data	397/4578	151/3129
ρ_{min}, ρ_{max}/e Å^{-3}	−0.39, 0.45	−0.24, 0.40
R_1	0.105 (0.039)[b]	0.060 (0.030)
wR_2	0.074 (0.063)[b]	0.062 (0.059)

[a] Details in common: monoclinic, space group $P2_1/n$ (no. 14); 150 K; [b] R_1 and wR_2 values for data with $I > 2\sigma(I)$ are given in parentheses. $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o)^2]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal paramaters and remaining bond lengths and angles.

Syntheses.—*Compound* **IIa** (R = Bu^n). Benzene (50 g, 0.32 mol) and aluminium chloride (25.4 g, 0.19 mol) were added to dichloromethane (500 cm^3) in a two-necked round-bottom flask equipped with a pressure-equalising dropping funnel, magnetic follower and a drying tube filled with calcium chloride. The flask was cooled in a salt–ice bath. To the yellow solution was added dropwise a solution of 2-bromohexanoyl bromide (50 g, 0.19 mol) dissolved in dichloromethane (50 cm^3). The solution gradually turned orange as the addition proceeded. After 12 h the solution was poured onto a mixture of cracked ice (1 kg) and concentrated HCl (100 cm^3) with vigorous stirring. The solution turned brown and then rapidly light yellow. Stirring was continued until the ice had melted. The organic phase was then removed using a separating funnel. The dichloromethane extract was dried over anhydrous magnesium sulfate and the solvent removed by rotary evaporation to yield a green-yellow oil (31.05 g, 64%) (Found: C, 57.30; H, 6.00. $C_{12}H_{15}BrO$ requires C, 56.50; H, 5.90). *m*/*z* (EI) 175 (40%, M^+ − Br). ^1H NMR (250 MHz $CDCl_3$): δ 8.9 (d, 2 H), 7.6 m, 1 H), 7.5 (m, 2 H), 5.7 (t, 1 H), 2.2 (m, 2 H), 1.5 (m, 4 H) and 1.0 (t, 3 H). IR: 1743 (C=O) and 1687 cm^{-1} (C=O).

Compound **IIIa** (R = Bu^n). To the α-bromo ketone **IIa** (19.00 g, 0.075 mol) dissolved in HPLC-grade acetone (500 cm^3) was added freshly recrystallised K[S_2COEt] (12.46 g, 0.077 mol) with vigorous stirring at room temperature. A white precipitate

Table 4 Atomic coordinates (× 10^4) for complex **1a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1							
Ni(1)	0*	0*	0*	C(6)	1145(5)	3396(6)	−2695(4)
S(1)	843(1)	993(1)	581(1)	C(7)	751(5)	3695(5)	−2047(4)
S(2)	95(1)	688(1)	−1047(1)	C(8)	646(5)	3150(5)	−1435(4)
C(1)	1103(4)	1766(5)	−91(3)	C(9)	1731(4)	2531(5)	196(3)
C(2)	780(4)	1633(5)	−822(3)	C(10)	1223(4)	3162(5)	723(3)
C(3)	923(4)	2246(5)	−1464(3)	C(11)	1863(5)	3864(5)	1103(3)
C(4)	1310(4)	1949(5)	−2134(3)	C(12)	1311(5)	4503(6)	1593(4)
C(5)	1419(5)	2502(6)	−2735(4)				
Molecule 2							
Ni(2)	3352.1(7)	−81.0(7)	96.8(4)	C(23)	5082(5)	3992(5)	767(4)
S(3)	4293(1)	926(1)	560(1)	C(24)	4561(5)	4642(5)	1273(4)
S(4)	3211(1)	601(1)	−956(1)	C(25)	2221(4)	−1798(5)	347(3)
S(5)	2358(1)	−1047(1)	−367(1)	C(26)	2735(4)	−1677(5)	1027(3)
S(6)	3487(1)	−778(1)	1150(1)	C(27)	2659(5)	−2311(5)	1676(3)
C(13)	4370(4)	1699(5)	−140(3)	C(28)	1802(5)	−2399(5)	2038(3)
C(14)	3893(4)	1548(5)	−836(3)	C(29)	1716(5)	−3002(5)	2614(3)
C(15)	3922(4)	2153(5)	−1499(3)	C(30)	2506(5)	−3550(5)	2824(3)
C(16)	4133(4)	1804(5)	−2202(3)	C(31)	3353(5)	−3465(5)	2479(3)
C(17)	4148(5)	2346(6)	−2839(4)	C(32)	3436(5)	−2848(5)	1903(3)
C(18)	3933(5)	3230(6)	−2786(4)	C(33)	1616(4)	−2612(4)	146(3)
C(19)	3688(5)	3589(5)	−2107(4)	C(34)	2207(5)	−3331(5)	−208(3)
C(20)	3678(4)	3053(5)	−1470(4)	C(35)	1670(4)	−4187(5)	−398(4)
C(21)	4997(5)	2509(5)	59(4)	C(36)	2307(5)	−4867(5)	−787(4)
C(22)	4504(5)	3157(5)	578(4)				

* Invariant parameter due to site-symmetry requirements.

Table 5 Atomic coordinates (× 10^4) for complex **1b**

Atom	*x*	*y*	*z*
Ni	0*	0*	0*
S(1)	2833(1)	−783(1)	471(1)
S(2)	−299(1)	−902(1)	−1051(1)
C(1)	3247(4)	−1670(2)	−226(2)
C(2)	1856(4)	−1712(2)	−923(1)
C(3)	2079(4)	−2419(2)	−1602(2)
C(4)	373(4)	−3064(2)	−1807(2)
C(5)	580(5)	−3711(2)	−2441(2)
C(6)	2461(5)	−3714(2)	−2888(2)
C(7)	4170(5)	−3076(2)	−2700(2)
C(8)	3983(4)	−2429(2)	−2061(2)
C(9)	4993(4)	−2427(2)	21(2)
C(10)	4184(4)	−3090(2)	686(2)
C(11)	2080(4)	−3635(2)	484(2)
C(12)	2011(5)	−4427(2)	1121(2)
C(13)	4420(5)	−4623(2)	1385(2)
C(14)	5819(4)	−3884(2)	950(2)

* Invariant parameter due to site-symmetry requirements.

formed immediately accompanied by a change of the solution from pale green to light yellow. The mixture was stirred for 1 h at room temperature with moisture excluded. The white precipitate of potassium bromide was filtered off. The acetone was removed from the filtrate by rotary evaporation to yield a light yellow oil (20.88 g, 93%) (Found: C, 61.45; H, 7.10. $C_{15}H_{20}O_2S_2$ requires C, 60.80; H, 6.80%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.0 (d, 2 H), 7.6 (m, 1 H), 7.5 (m, 2 H), 5.5 (t, 1 H), 4.6 (q, 2 H), 2.1 (m, 1 H), 1.9 (m, 1 H), 1.4 (m, 7 H) and 0.9 (t, 3 H). IR: 1744 (C=O), 1683 (C=O), 1225 (C–O) and 1050 cm^{-1} (C–O).

Compound **IVa** (R = Bu^n). To a flask containing concentrated sulfuric acid (50 cm^3) at 0 °C in an ice-bath was added the xanthate ester **IIIa** (21.0 g, 0.071 mol) from the previous preparation with vigorous stirring. The light yellow oil darkened immediately upon contact with concentrated acid. The reaction mixture was stirred for 5 h then poured onto cracked ice. The organic phase was extracted with dichloromethane (2 × 100 cm^3), dried over anhydrous $MgSO_4$, filtered and the solvent removed by rotary evaporation. A red oil was obtained which was purified by column chromatography on silica (conditioned with light petroleum, b.p. 40–60 °C) using CH_2Cl_2 as eluent. A red impurity remained at the top of the column and the product passed down the column as a broad yellow band which was collected. The solvent was removed on a rotary evaporator to yield the purified material as an orange oil (7.35 g, 41.3%) (Found: C, 61.70; H, 5.55. $C_{13}H_{14}OS_2$ requires C, 62.35; H, 5.65%). *m*/*z* (EI) 250 (100%, M^+). ^1H NMR (250 MHz, $CDCl_3$): δ 7.4 (m, 5 H), 2.6 (t, 2 H), 1.4 (m, 6 H) and 0.9 (t, 3 H). IR 1643 cm^{-1} (C=O).

Complex **1a** (R = Bu^n). Sodium (0.31 g, 0.014 mol) was dissolved in dry degassed ethanol (30 cm^3) under an argon blanket. To the sodium ethoxide solution was added compound **IVa** (1.06 g, 4.23 mmol) and the mixture stirred for 1 h at room temperature. To the yellow solution of the disodium salt was added dropwise with stirring tetraethylammonium bromide (1.81 g, 8.6 mmol) dissolved in dry degassed ethanol (20 cm^3) followed dropwise with stirring by a solution of $NiCl_2 \cdot 6H_2O$ (0.45 g, 1.9 mmol) dissolved in dry degassed ethanol (20 cm^3) over a period of 90 min. The formation of the dianionic nickel complex was accompanied by a change in the solution from yellow to reddish brown. As addition of the nickel salt proceeded a reddish brown precipitate formed. After the addition was complete the flask was stoppered and placed in a freezer at −30 °C overnight. The brick-red powder was filtered off and washed with ice-cold ethanol, yield 0.93 g (1.2 mmol, 28.4%, based on ligand). The red powder was dissolved in acetone, filtered and to the red solution was added dropwise with stirring a solution of iodine (0.31 g, 2.5 mmol) dissolved in acetone (30 cm^3). The acetone was removed from the green solution by rotary evaporation and the resulting green oil dissolved in dichloromethane (100 cm^3) and filtered. To the green solution was added methanol (50 cm^3) and the volume reduced by *ca.* 2/3 on a rotary evaporator. The flask was then placed in a freezer set at −30 °C. The product was obtained as fine dark blue needles. This procedure was repeated to yield the purified product (0.43 g, 20% based on ligand) (Found: C, 57.30; H, 5.80. $C_{24}H_{28}NiS_4$ requires C, 57.25; H, 5.60%). ^1H NMR (250 MHz, $CDCl_3$): δ 7.5 (s, 10 H), 2.9 (t, 4 H), 1.7 (m, 4 H), 1.3 (m, 4 H) and 0.9 (t, 6 H). IR: 1373 cm^{-1}.

Compound **Ib** (R = $CH_2C_5H_9$). This compound was prepared by the Friedel–Crafts acylation of 3-cyclopentylpropionyl chloride (10 g, 0.06 mol) with benzene (4.9 g, 0.06 mol) in the presence of aluminium trichloride (8.30 g, 0.06 mol). Upon work-up the product was obtained as an orange oil. This was purified by column chromatography on silica (conditioned with light petroleum, b.p. 40–60 °C) using light petroleum–dichloromethane (1 : 1) as eluent. The product was obtained as an orange oil (11.67 g, 92%) (Found: C, 81.45; H, 9.55. $C_{14}H_{18}O$ requires C, 83.20; H, 8.90%). *m*/*z* (EI) 202 (30%, M^+). ^1H NMR (250 MHz, $CDCl_3$): δ 7.9 (d, 2 H), 7.5 (m, 1 H), 7.4 (m, 2 H), 2.98 (t, 2 H), 1.7 (m, 6 H) and 1.5 (m, 5 H). IR: 1685 cm^{-1} (C=O).

Compound **IIb** (R = $CH_2C_5H_9$). The ketone **Ib** (5.05 g, 0.02 mol) from the above reaction was dissolved in dichloromethane (50 cm^3) and bromine (3.99 g, 0.02 mol) dissolved in dichloromethane was added dropwise with stirring. Moisture was excluded throughout the reaction. The bromine colour disappeared immediately from the solution and after all the bromine had been added the solution was stirred for 30 min. The solvent was removed *in vacuo* (**CAUTION**: HBr fumes!) to yield a golden-yellow oil (6.41 g, 90%) (Found: C, 60.00; H, 7.35. $C_{14}H_{17}BrO$ requires C, 59.80; H, 6.10%). *m*/*z* (EI) 201 (20%, M^+ − Br).

Compound **IIIb** (R = $CH_2C_5H_9$). The α-bromo ketone **IIb** (5 g, 0.02 mol) was dissolved in ethanol (60 cm^3) and freshly recrystallised K[S_2COEt] (2.85 g, 0.02 mol) added. Upon work-up the product was obtained as a yellow oil (5.33 g, 93%) (Found: C, 64.55; H, 6.35. $C_{17}H_{22}O_2S_2$ requires C, 63.30; H, 6.90%). IR: 1682 (C=O) and 1049 cm^{-1} (C–O).

Compound **IVb** (R = $CH_2C_5H_9$). The yellow oil **IIIb** (5.00 g, 15 mmol) from the previous reaction was added to vigorously stirred concentrated H_2SO_4 (40 cm^3) at 0 °C. After 1 h the mixture was poured onto ice (500 g) and the crude compound extracted with diethyl ether (3 × 150 cm^3). The organic phase was dried over anhydrous magnesium sulfate and the solution filtered. The solvent was removed by rotary evaporation to yield a dark red oil This was dissolved in the minimum volume of dichloromethane and purified by flash column chromatography (CH_2Cl_2 eluent) on silica conditioned with light petroleum to provide an orange oil (3.56 g, 80%) (Found: C, 63.65; H, 6.85. $C_{15}H_{16}OS_2$ requires C, 65.20; H, 5.80%). *m*/*z* (EI) 276 (55%, M^+). IR: 1650 cm^{-1} (C=O).

Complex **1b** (R = $CH_2C_5H_9$). Compound **IVb** (1.5 g, 5 mmol) was dissolved in dry ethanol (30 cm^3) under an argon blanket to give a red solution. To this solution was added sodium (0.67 g, 30 mmol) dissolved in dry ethanol (15 cm^3) and the mixture stirred at room temperature for 30 min. Tetra-*n*-butylammonium bromide (3.68 g, 11 mmol) dissolved in dry ethanol (15 cm^3) was added, followed dropwise by a solution of $NiCl_2 \cdot 6H_2O$ (0.67 g, 2 mmol) in dry ethanol (15 cm^3). The clear dark brown solution was concentrated *in vacuo* and the resultant sludge redissolved in acetone (30 cm^3) and filtered. Iodine (0.68 g, 5 mmol) dissolved in acetone (20 cm^3) was added to the stirred solution resulting in the instantaneous formation of a dark green solution. Reduction of the solvent volume *in vacuo* afforded a black solid which was filtered off, washed with ethanol and dried. Recrystallisation from dichloromethane–methanol afforded the pure product as a blue–black crystalline solid (0.42 g, 30%), m.p. 204–205 °C (Found: C, 59.40; H, 5.90. $C_{28}H_{32}NiS_4$ requires C, 58.80; H, 6.00%). *m*/*z* (EI) 554 (70%,

M^+ − H). IR (KBr): 2867 (C–H), 1376 (C–C), 1177 (C–S) and 514 cm^{-1} (Ni–S).

(4-Pentylcyclohexyl)ethanoyl chloride. (4-Pentylcyclohexyl)ethanoic acid (5.00 g, 0.023 mol) was dissolved in freshly distilled thionyl chloride (20 cm^3) under an argon blanket. The mixture was stirred at room temperature for 20 min and then refluxed for 4 h to yield a dark yellow solution. Removal of the excess of thionyl chloride under vacuum afforded an orange oil (5.20 g, 95%). The product was used without further purification.

Compound **Ic** (R = $C_5H_{11}C_6H_{10}$). (4-Pentylcyclohexyl)ethanoyl chloride (5.20 g, 0.022 mol) was dissolved in dry dichloromethane (60 cm^3) and benzene (1.76 g, 0.022 mol) added. This mixture was stirred in a flask in a salt–ice bath for 30 min with moisture excluded ($CaCl_2$ drying tube). Aluminium chloride (3.00 g, 0.022 mol) was then added cautiously. An instant change from colourless to red-brown was observed and the mixture was left stirring overnight. Acid work-up yielded an orange oil. This was recrystallised from boiling methanol to afford the product as a white powder (4.96 g, 80%). *m/z* (EI) 272 (35%, M^+). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.0 (d, 2 H), 7.5 (m, 1 H), 7.4 (d, 2 H), 2.8 (d, 2 H), 1.7 (m, 4 H), 1.2 (m, 10 H), 1.0 (m, 3 H) and 0.9 (t, 3 H).

Compound **IIc** (R = $C_5H_{11}C_6H_{10}$). The ketone **Ic** (2.5 g, 9.2 mmol) was dissolved in dry dichloromethane (40 cm^3) and bromine (1.47 g, 9.2 mmol) dissolved in dichloromethane (20 cm^3) added dropwise. The mixture was stirred at room temperature for 1 h and then refluxed for 6 h. The solvent was removed by rotary evaporation to yield a golden-brown oil. This solidified upon cooling and was recrystallised from boiling methanol to yield a white waxy solid (2.86 g, 88%) (Found: C, 64.40; H, 7.20. $C_{19}H_{17}BrO$ requires C, 65.00; H, 7.75%). *m/z* (EI) 351 (20, M^+) and 271 (55%, M^+ − Br). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.0 (d, 2 H), 7.5 (m, 1 H), 7.4 (d, 2 H), 4.9 (d, 1 H), 1.7 (m, 4 H), 1.2 (m, 10 H), 1.0 (m, 3 H) and 0.9 (t, 3 H). IR (CH_2Cl_2): 1686 cm^{-1} (C=O).

Compound **IIIc** (R = $C_5H_{11}C_6H_{10}$). The α-bromo ketone **IIc** (1.5 g, 4.3 mmol) was dissolved in ethanol (50 cm^3) and $K[S_2COEt]$ (0.68 g, 4.3 mmol) added. The mixture was refluxed for 2 h during which a change to orange-brown was observed. The white precipitate was filtered off and washed with ethanol. Removal of the solvent from the filtrate yielded an orange-brown oil (1.38 g, 82%) (Found: C, 69.25; H, 8.35. $C_{22}H_{32}O_2S_2$ requires C, 67.30; H, 8.2%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.0 (d, 2. H), 7.5 (m, 1 H), 7.4 (d, 2 H), 5.5 (d, 1 H), 4.6 (q, 2 H), 2.0 (m, 2 H), 1.7 (m, 2 H), 1.3 (m, 13 H) and 0.9 (t, 6 H).

Compound **IVc** (R = $C_5H_{11}C_6H_{10}$). The xanthate intermediate **IIIc** (1.16 g, 3 mmol) was dissolved in ice-cold concentrated H_2SO_4 (60 cm^3). The mixture was stirred for 1 h and the golden-yellow solution poured onto ice (500 g). The product was extracted with diethyl ether (2 × 200 cm^3). The organic phase was dried over magnesium sulfate and concentrated *in vacuo* to yield a yellow oil (0.83 g, 80%) (Found: C, 62.35; H, 6.00. $C_{20}H_{26}OS_2$ requires C, 61.80; H, 6.75%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.4 (m, 5 H), 1.8 (m, 5 H), 1.3 (m, 13 H) and 0.9 (t, 3 H).

Complex **1c** (R = $C_5H_{11}C_6H_{10}$). Compound **IVc** (0.70 g, 2 mmol) was suspended in dry methanol (20 cm^3) under an argon blanket. Sodium (0.09 g, 4 mmol) dissolved in methanol (10 cm^3) was added and an instantaneous change from yellow to dark brown was observed. The mixture was refluxed for 1 h and then $NBu^n{}_4Br$ (0.65 g, 2 mmol) dissolved in methanol (10 cm^3) was added. A solution of $NiCl_2{\cdot}6H_2O$ (0.24 g, 1 mmol) dissolved in methanol (30 cm^3) was then added dropwise with vigorous stirring. After 1 h the solvent was removed by rotary evaporation to yield an oily brown solid which was redissolved in acetone (30 cm^3) and filtered. Iodine (0.25 g, 2 mmol) in acetone (20 cm^3) was then added to the solution with stirring. The solvent volume was reduced by *ca.* $\frac{1}{2}$ and the solution placed in a freezer at −30 °C for 2 h. A black precipitate formed which was collected, washed with acetone and air dried. Recrystallisation from CH_2Cl_2–MeOH afforded the pure metal complex as a dark green microcrystalline solid (0.09 g, 6.5%), m.p. 197–199 °C (Found: C, 64.80, H, 6.75. $C_{38}H_{52}NiS_4$ requires C, 65.65; H, 7.45%). *m/z* (EI) 694 (100%, M^+). IR (KBr): 2852 (C–H), 1380 (C–C), 1178 (C–S) and 521 cm^{-1} (Ni–S).

Acknowledgements

We thank BT (Martlesham) for financial support and for a CASE studentship (for A. C.) and the SERC for support of the X-Ray Crystallography Service at Cardiff.

References

1 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.

2 U. T. Mueller-Westerhoff, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1986, vol. 2, p. 595.

3 U. T. Mueller-Westerhoff, B. Vance and D. I. Yoon, *Tetrahedron*, 1991, **47**, 909.

4 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115.

5 N. D. Lowe and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1993, 2197.

6 C. S. Winter, S. N. Oliver, R. J. Manning, J. D. Rush, C. A. S. Hill and A. E. Underhill, *J. Mater. Chem.*, 1992, **2**, 443.

7 A. E. Underhill, C. A. S. Hill, C. S. Winter, S. N. Oliver and J. D. Rush, *Mol. Cryst. Liq. Cryst.*, 1993, **217**, 7.

8 C. S. Winter, S. N. Oliver, J. D. Rush, C. A. S. Hill and A. E. Underhill, *Organic Molecules for Nonlinear Optics and Photonics*, eds. J. Messier, F. Kajzar and P. N. Prasad, Kluwer Academic Publishers, Dordrecht, 1991, pp. 383–390.

9 C. S. Winter, S. N. Oliver, J. D. Rush, C. A. S. Hill and A. E. Underhill, *Mol. Cryst. Liq. Cryst.*, 1993, **235**, 181.

10 S. N. Oliver, C. S. Winter, R. J. Manning, J. D. Rush, C. A. S. Hill and A. E. Underhill, *SPIE J.*, 1992, **1775**, 110.

11 M. Kodaka, T. Fukaya, K. Yonemoto and I. Shibya, *J. Chem. Soc., Chem. Commun.*, 1990, 1096.

12 U. T. Mueller-Westerhoff, A. Nazzal, R. J. Cox and A. M. Giroud, *Mol. Cryst. Liq. Cryst. (Lett.)*, 1980, **56**, 249.

13 Z. S. Herman, R. F. Kirchner, G. M. Loew, U. T. Mueller-Westerhoff, A. Nazzal and M. C. Zerner, *Inorg. Chem.*, 1982, **21**, 46.

14 G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1983, **22**, 1208.

15 D. C. Olson, V. P. Mayweg and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1966, **88**, 4876.

16 C. S. Winter, S. N. Oliver, J. D. Rush, C. A. S. Hill and A. E. Underhill, *J. Appl. Phys.*, 1992, **71**, 512.

17 S. N. Oliver, S. V. Kershaw, B. J. Ainslie, A. E. Underhill, C. A. S. Hill and A. Charlton, *Nonlinear Opt.*, in the press.

18 M. Cotrait, J. Gaultier, C. Polycarpe, A. M. Giroud and U. T. Mueller-Westerhoff, *Acta Crystallogr., Sect. C*, 1983, **39**, 833.

19 W. E. Williams, M. J. Soileau and E. W. Van Stryland, *Opt. Commun.*, 1984, **50**, 256.

20 K. J. Witte, M. Galanti and R. Volk, *Opt. Commun.*, 1980, **34**, 278.

21 G. M. Carter, *J. Opt. Soc. Am.*, 1987, **4**, 1018.

22 J. A. Darr, S. R. Drake, M. B. Hursthouse and K. M. A. Malik, *Inorg. Chem.*, 1993, **32**, 5704.

23 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

24 G. M. Sheldrick, SHELXL 93 Program System, University of Göttingen, 1993.

25 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158; adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff, 1991.

Received 30*th August* 1994; *Paper* 4/05256K