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Bis(1,2-(substituted diphenyl)-1,2-ethanedithiolato)nickels having High Solubility

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ABSTRACT

The solubilities of bis(1,2-diphenyl-1,2-ethanedithiolato)nickels in benzene are effectively improved by introduction of substituent groups in the o,o'-position of the phenyl rings. The structure of a crystalline form of bis[1,2-(3,5-dimethoxy-4-butoxyphenyl)-1,2-ethanedithiolato]nickel having the highest solubility has been determined by single-crystal X-ray diffraction analysis. Comparison of this crystal structure with two known forms of bis(1,2-diphenyl-1,2-ethanedithiolato)nickel indicates that the high solubility is basically due to a longer interplane spacing between the parallel chelate planes of the adjacent molecules, which results in interaction of the methoxy substituents lying in the same plane as the phenyl ring.

1 INTRODUCTION

Dithiolene nickel complexes are known to be effective as quenchers of singlet oxygen,[1] with which organic dyes can react, leading to permanent fading. Recently, these complexes have been studied with respect to their use in

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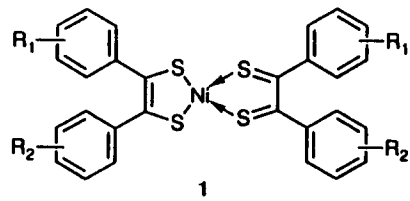

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stabilizers for optical data storage systems using cyanine dyes.[2,3] In practical systems, the solubility of such stabilizers in an organic solvent is important, since the recording thin layer is formed by a spin-coating technique.[4]

We have shown that introduction of alkoxy groups at the 3,4,5-positions in the phenyl rings of bis(1,2-diphenyl-1,2-ethanedithiolato)nickel leads to high solubility[5] and have now found that the 3,5-dimethoxy-4-butoxy substituted derivative (**1e**) shows the highest solubility. Herein, we determined its full structure by single-crystal X-ray diffraction analysis and compared it with previously known unsubstituted nickel complexes.[6,7]

2 RESULTS AND DISCUSSION

2.1 Solubility

The solubility parameters of organic dyes and stabilizers in optical data storage systems are very important, since the recording layer is formed by the spin-coating technique.

The solubilities of nickel complex **1** in benzene are summarized in Table 1.

TABLE 1
Solubility of Nickel Complexes **1** in Benzene at 25°C

Compd	$R^1 = R^2$	*Solubility (wt%)*	λ_{max} *(nm)*[a]	*Ref.*
1a	H	0·13	855	8
1b	4-MeO	0·12	926	8
1c	4-Me	0·15	878	8
1d	3,4,5-$(MeO)_3$	4·4	925	5
1e	4-BuO-3,5-$(MeO)_2$	7·6	933	This work
1f	4-Bu	3·1	886	This work
1g	2-Me	0·74	812	5
1h	2,4-$(Cl)_2$	4·5	787	8
1i	2-Cl	0·56	783	8
1j	2-Br	1·5	783	8

[a] In CH_2Cl_2.

We have previously reported that solubility is very effectively improved with a hypsochromic shift of the absorption band in the near-IR region, by introducing a halogen substituent into the 2-position of the phenyl rings of **1**.[8] The solubility of the nickel complex **1** is also improved by introducing a longer alkoxy or alkyl group into the phenyl ring, as, for example, in **1f**. Comparison between **1b** and **1d** shows that introduction of methoxy groups into the 3- and 5-positions of the phenyl rings leads to high solubility. The 3,5-dimethoxy substituted derivative (**1e**), which also contains a higher alkoxy group at the 4-position, shows the highest solubility. The methoxy substituents in the *o,o'*-positions of the phenyl rings of **1** thus contribute significantly to the high solubility.

2.2 Molecular structure of 1e

The structure of **1e** was compared with the previously established two phases of **1a**. The ORTEP drawing[10] for **1e**, with atom numbering, is shown in Fig. 1. The conformation of **1e** shows a $\bar{1}$ symmetry. The bond lengths and bond angles of **1e**, and the position coordinates, are given in Tables 2, 3 and 4, respectively. The bond distances of Ni—S, S—C, and C=C in the chelate plane of **1e** are the same as those of α- and β-**1a**; however, the C(1)–C(3) bond distance is longer compared with α- and β-**1a**, as shown in Table 5. The C3 atom deviates by 0·11 Å from the chelate plane 1, as shown in Table 6. This longer bond length might arise from steric hindrance between the 5-methoxy and 3'-methoxy groups in neighboring phenyl groups.

The chelate ring of **1e**, as well as **1a**, is planar and the connected carbon atoms [C1–C2 and C15] lie on the same plane as the chelate ring, except for

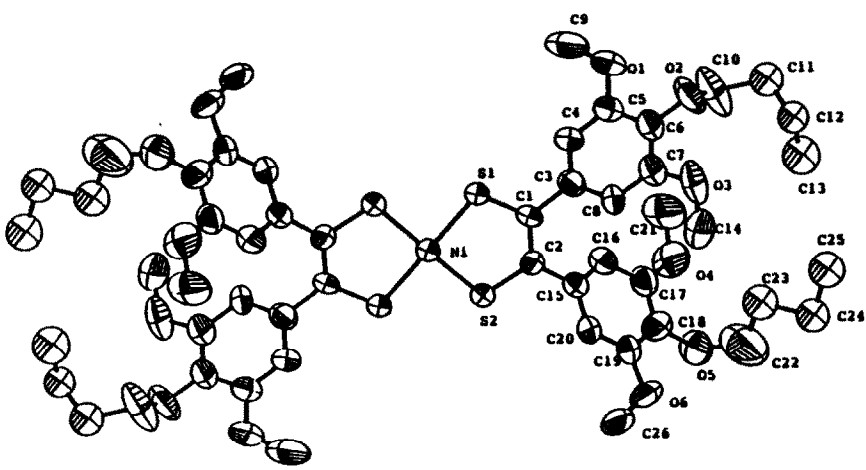

Fig. 1. ORTEP drawing for **1e** with atom numbering.

TABLE 2
Selected Bond Lengths[a] (Å) of **1e**

Ni—S1	2·113 (5)	Ni—S2	2·124 (5)
S1—C1	1·692 (16)	S2—C2	1·688 (16)
C1—C2	1·386 (22)	C1—C3	1·524 (22)
C2—C15	1·480 (22)	C3—C4	1·363 (23)
C3—C8	1·398 (23)	C4—C5	1·386 (26)
C5—C6	1·398 (26)	C6—C7	1·381 (25)
C7—C8	1·395 (24)	C15—C16	1·417 (22)
C15—C20	1·380 (23)	C16—C17	1·386 (23)
C17—C18	1·379 (23)	C18—C19	1·396 (24)
C19—C20	1·370 (23)	C10—C11	1·540 (33)
C11—C12	1·398 (33)	C12—C13	1·364 (37)
C22—C23	1·399 (45)	C23—C24	1·605 (35)
C24—C25	1·468 (37)	O1—C5	1·391 (23)
O1—C9	1·390 (26)	O2—C6	1·379 (21)
O2—C10	1·506 (25)	O3—C7	1·343 (21)
O3—C14	1·410 (23)	O4—C17	1·370 (20)
O4—C21	1·399 (25)	O5—C18	1·382 (21)
O5—C22	1·484 (39)	O6—C19	1·405 (22)
O6—C26	1·364 (27)		

[a] Estimated standard deviations are given in parentheses.

TABLE 3
Selected Bond Angles[a] (°) of **1e**

S1—Ni—S2	91·3 (2)	Ni—S1—C1	105·0 (6)
Ni—S2—C2	105·6 (6)	S1—C1—C2	119·9 (12)
S2—C2—C1	118·3 (12)	C2—C1—C3	124·4 (14)
C1—C2—C15	124·1 (14)	C3—C4—C5	119·3 (16)
C4—C5—C6	119·4 (17)	C5—C6—C7	121·0 (17)
C6—C7—C8	119·5 (16)	C7—C8—C3	118·4 (15)
C8—C3—C4	122·3 (15)	C15—C16—C17	119·7 (15)
C16—C17—C18	120·1 (15)	C17—C18—C19	119·4 (15)
C18—C19—C20	121·5 (15)	C19—C20—C15	119·6 (15)
C20—C15—C16	119·7 (15)	C5—O1—C9	119·7 (16)
C7—O3—C14	118·4 (14)	C6—O2—C10	112·3 (14)
O2—C10—C11	108·1 (17)	C10—C11—C12	114·2 (20)
C11—C12—C13	117·7 (22)	C17—O4—C21	119·9 (14)
C19—O6—C26	117·1 (15)	C18—O5—C22	124·0 (18)
O5—C22—C23	118·5 (28)	C22—C23—C24	101·6 (23)
C23—C24—C25	98·4 (20)		

[a] Estimated standard deviations are given in parentheses.

TABLE 4
Final Atomic Parameters[a] ($\times 10^4$) of **1e**

Atom	*x*	*y*	*z*
Ni	0	0	0
S1	82 (3)	1 163 (3)	531 (6)
S2	1 076 (2)	6 (3)	−652 (6)
C1	924 (8)	1 422 (7)	130 (20)
C2	1 384 (7)	891 (8)	−410 (20)
C3	1 147 (8)	2 234 (8)	550 (20)
C4	679 (9)	2 798 (8)	−40 (30)
C5	887 (9)	3 541 (9)	260 (30)
C6	1 580 (9)	3 700 (9)	1 120 (30)
C7	2 053 (9)	3 126 (9)	1 700 (20)
C8	1 839 (8)	2 377 (8)	1 420 (20)
C9	−270 (20)	4 030 (10)	−1 040 (30)
C10	2 000 (20)	4 820 (10)	−20 (30)
C11	2 550 (20)	5 460 (20)	540 (30)
C12	3 250 (20)	5 210 (20)	1 170 (30)
C13	3 670 (20)	4 890 (20)	180 (40)
C14	3 228 (9)	2 770 (20)	3 020 (30)
C15	2 113 (8)	1 067 (8)	−880 (20)
C16	2 186 (8)	1 710 (8)	−1 820 (20)
C17	2 867 (8)	1 882 (8)	−2 260 (20)
C18	3 463 (8)	1 413 (9)	−1 830 (20)
C19	3 379 (8)	777 (8)	−910 (20)
C20	2 715 (8)	605 (8)	−440 (20)
C21	2 410 (20)	3 050 (10)	−3 450 (30)
C22	4 730 (20)	2 020 (20)	−1 440 (50)
C23	4 540 (20)	2 680 (20)	−720 (30)
C24	5 340 (20)	2 990 (20)	50 (30)
C25	5 100 (20)	3 670 (20)	810 (40)
C26	3 967 (9)	−327 (9)	190 (30)
O1	441 (6)	4 154 (6)	−260 (20)
O2	1 794 (7)	4 438 (6)	1 420 (20)
O3	2 704 (7)	3 332 (7)	2 530 (20)
O4	2 955 (6)	2 488 (7)	−3 210 (20)
O5	4 132 (7)	1 560 (7)	−2 340 (20)
O6	4 028 (6)	351 (6)	−530 (20)

[a] Standard deviations referring to the least significant figure for each term are given in parentheses.

C3. The phenyl ring and the methoxy groups lie on the same plane, as is clearly indicated by Table 6. The dihedral angles between the chelate ring (plane 1) and a phenyl ring (plane 2 or plane 3) are 45·5° and 48·7°, respectively. At least one of these dihedral angles is larger, compared with unsubstituted derivative **1a**,[6,7] as shown in Fig. 2.

TABLE 5
Selected bond lengths[a] (Å) of **1e**, α- and β-**1a**

Bond	**1e**	α-**1a**[b]	β-**1a**[c]
Ni—S	2·113 (5)	2·096 (2)	2·120 (1)
	2·124 (5)	2·105 (2)	2·125 (1)
			2·125 (1)
			2·127 (1)
S—C	1·688 (16)	1·693(8)	1·695 (4)
	1·692 (16)	1·725 (8)	1·701 (4)
			1·702 (4)
			1·718 (4)
C=C	1·386 (22)	1·373 (14)	1·404 (6)
			1·424 (6)
C1—C3 or	1·524 (22)	1·454 (11)	1·474 (6)
C2—C15	1·480 (22)	1·478 (11)	1·482 (5)
			1·484 (5)
			1·484 (5)

[a] Estimated standard deviations are given in parentheses.
[b] Ref. 6.
[c] Ref. 7.

TABLE 6
Deviations (Å) from the Optimum Planes 1–3 in **1e**

Atom	*Deviation from plane 1*[a]	*Atom*	*Deviation from plane 2*[b]	*Atom*	*Deviation from plane 3*[c]
Ni	0·000	C15	−0·005	C3	0·002
S1	0·008	C16	0·012	C4	−0·007
S2	0·007	C17	−0·010	C5	0·009
C1	−0·004	C18	0·002	C6	−0·005
C2	−0·003	C19	0·004	C7	−0·002
		C20	−0·002	C8	0·004
C3	0·115	C2	0·017	C1	−0·090
C15	−0·083	O4	0·039	O1	0·027
		O5	0·057	O2	0·002
		O6	−0·001	O3	−0·002

[a] Plane 1: Ni—S1—C1—C2—S2.
[b] Plane 2: C15—C16—C17—C18—C19—C20.
[c] Plane 3: C3—C4—C5—C6—C7—C8.

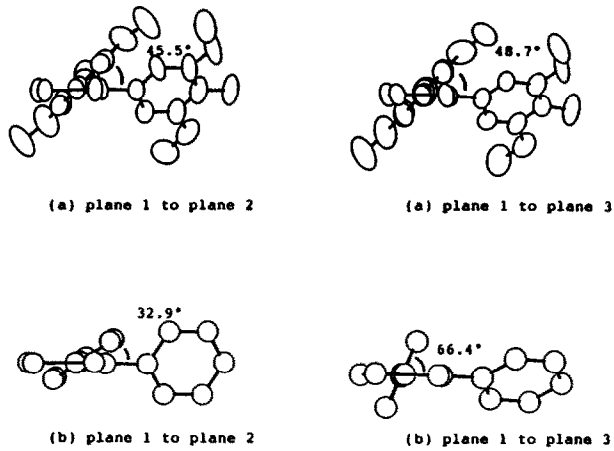

Fig. 2. Dihedral angles between the chelate ring and the phenyl rings of the nickel complexes: (a) **1e**; (b) α-**1a** (β-**1a**: 34·8°, 44·7°, 50·7°, and 53·0°).

Increase of dihedral angle and the increased separation of methoxy groups at the 3- and 5′-positions of the coplanar phenyl rings would be expected to result in inhibition of intermolecular aggregation among the chelate planes of **1**. It was found experimentally that the molecules, in the case of **1e**, are overlapped in a large stack, in which the interplanar spacing between parallel chelate planes of the adjacent molecules is 7·68 Å. This interplanar spacing in **1e** is significantly greater than the value of 4·07 and *c.* 4·30 Å found for unsubstituted nickel complexes α- and β-**1a**,[6,7] respectively, as shown in Table 7.

The butoxy groups are arranged face-to-face to each other, and their intermolecular interaction is almost absent on the *ab* and *ac* planes. The most adjacent substituent groups in the packing diagram are the two methoxy groups at the *3*- and *5*-positions of **1e** with an intermolecular distance of 3·38 Å; the intermolecular distance between the C26 atom in the

TABLE 7

Deviations (Å) from the Optimum Planes of the Chelate Ring (Plane 1) in **1e**, α- and β-**1a** to the Parallel Neighboring Molecule

Atom	**1e**	α-**1a**	β-**1a**
Ni	7·67	4·07	4·37
S	7·68	4·07	4·29
	7·68	4·07	4·29
			4·35
			4·35

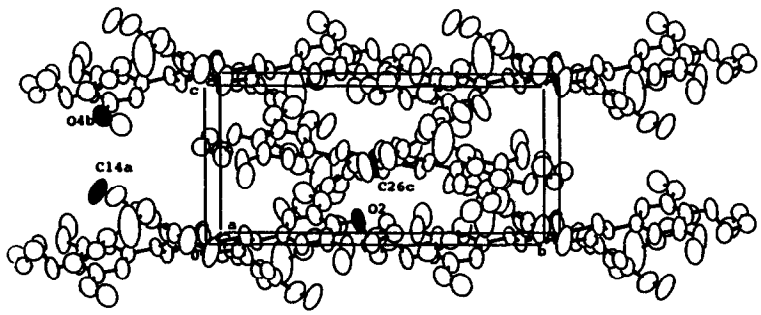

Fig. 3. Packing diagram of **1e**. Symmetry code: a, $-x, -y, -z$; b, $-x, -y, 1-z$; c, $0{\cdot}5-x$, $0{\cdot}5+y$, $0{\cdot}5-z$, O2–C26c: 3·43 Å, C14a–C4b: 3·38 Å.

methoxy group and the O(2) atom in the butoxy group is also close to 3·40 Å, as shown in Fig. 3.

Thus, the higher solubility of **1e** might be mainly due to the loss of overlap between the intermolecular chelate planes due to the methoxy substituents, and not to butoxy groups. It is suggested that the introduction of substituent groups which increase the dihedral angles between the phenyl groups and the five-membered nickel chelate plane leads to higher solubility. The nickel complexes **1h** and **1d** with halogen atoms and methoxy groups at such positions also show high solubility due to this steric hindrance.

3 EXPERIMENTAL

3.1 Solubility

Suspensions of the nickel complexes[1,2,5,8] in benzene were kept at 25°C for 1 h until the solutions were saturated. The solutions were then filtered through a membrane filter (mesh 0·2 μm) and the solubility at 25°C was determined spectrophotometrically after dilution of the saturated solution.

3.2 X-ray crystallography

The crystal of **1e** was obtained by slow recrystallization from saturated ethanol–chloroform (20:1, v/v) at 35°C. All data were collected at 23°C on a Rigaku AFC-6R diffractometer with graphite-monochromated Mo–Kα radiation in the range $2\theta < 50°$ of the ω–2θ scan mode; 1805 reflections had $F > 3\sigma(F)$ and were used in the structure refinement. The structure was solved by the Paterson method and completed by block-diagonal Fourier using the UNICS program[9] of Osaka University.

The non-hydrogen atoms in **1e**, except for the three carbon atoms in the

butoxy groups, were assigned anisotropic thermal parameters. The isotropic treatments for the carbon atoms in the butoxy group are due to the large isotropic parameters (B_{jj}) which are reduced to half-values in the ORTEP drawing. All hydrogen atoms were placed in calculated positions and included in the structure factor. The final conventional indexes R and R_w are 0·110 and 0·098, respectively.

Crystal data

$C_{52}H_{68}NiO_{12}S_4$, $M = 1072{\cdot}06$, Monoclinic, Space group $P2_1/n$, $a = 18{\cdot}298(4)$, $b = 17{\cdot}728(4)$, $c = 8{\cdot}566(9)$ Å, $\beta = 98{\cdot}38(4)°$, $V = 2749$ Å^3, $Z = 2$, $d_c = 1{\cdot}30$ g cm^{-3}, crystal size 0·5 mm × 0·2 mm × 0·15 mm.

Tables of final atomic parameters including hydrogen atoms, anisotropic and isotropic parameters, and the F_o–F_c table are available on request from the publisher.

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