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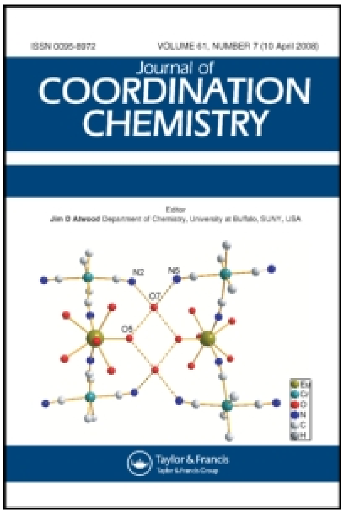

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Synthesis, Structures and Dynamic Properties of Trimethylene- And Tetramethylene-Bis(*CIS*-Stilbene-1,2-Dithiolato)Nickel(II)

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SYNTHESIS, STRUCTURES AND DYNAMIC PROPERTIES OF TRIMETHYLENE- AND TETRAMETHYLENE-BIS(*CIS*-STILBENE-1,2-DITHIOLATO)NICKEL(II)

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The unusual, structurally dynamic behaviour of the Ni(II) dialkyldithiolene Ni[$(CH_3)_2S_4Ph_4$], **1**, in solution prompted a study of the related macrocyclic complexes, Ni[$(CH_2)_3S_4C_4Ph_4$], **2**, and Ni[$(CH_2)_4S_4C_4Ph_4$], **3**, whose synthesis, structures and dynamic properties in solution are described. Complex **2**, isolated as a $CHCl_3$ inclusion compound, crystallizes in space group *C*2/*c* with 8 molecules per unit cell, $a = 29.26(2)$, $b = 8.170(4)$, $c = 30.76(2)$ Å, $\beta = 116.69(6)°$. The complex has the *cis-syn* configuration with respect to the Ni-S(CH_2)- bonds and the coordination geometry of Ni is essentially square planar, with mean Ni-S and Ni-S(CH_2) bond lengths of 2.174(4) and 2.162(5) Å, respectively. Complex **3** crystallizes in space group $P2_1/n$, with 4 molecules per unit cell, $a = 10.07(1)$, $b = 18.22(2)$ Å, $c = 15.36(2)$ Å, $\beta = 94.56(8)°$, and the Ni-S(CH_2)- bonds are in the *cis-anti*-configuration. The mean Ni-S- and Ni-S(CH_2) bond lengths are 2.156(5) and 2.153(9) Å, respectively. The coordination geometry of Ni is slightly tetrahedrally distorted from planar, with bond angles S-Ni-S of 87.6(1)°, (CH_2)S-Ni-S(CH_2), 97.7(1)° and the mean of S-Ni-S(CH_2) bond angles 162(2)°. The ^1H NMR spectrum of **2** in CD_2Cl_2 shows the presence only of the one isomer and is temperature independent between $-50°$ and $+50°C$. The ^1H NMR spectrum of **3** is temperature dependent due to dynamic equilibrium between the *cis-anti-* and *cis-syn*-isomers.

Keywords: Trimethylene-bis(*cis*-stilbene-1,2-dithiolato)nickel(II), tetramethylene-bis(*cis*-stilbene-1,2-dithiolato)nickel(II), dithiolene complexes, dialkyldithiolene complexes, X-ray structures

INTRODUCTION

In recent papers[1,2] we showed that the *S,S'*-dimethyl and dibenzyl derivatives of *bis*(*cis*-stilbene-1,2-dithiolato)nickel(II), palladium(II) and platinum(II) of composition M[$R_2S_4C_4Ph_4$] (M = Ni, Pd, Pt, R = CH_3 or CH_2Ph) have the *trans-anti* configuration in the solid state and are structurally dynamic in solution due to sulfur inversion and *cis-trans* isomerization reactions. The Ni(II) complex with R = CH_3, **1**, for example, was found to exist in CD_2Cl_2 at $-50°C$ as a mixture of 3 interchangeable species which were assigned to be *trans-anti*, *trans-syn* and *cis-anti* isomers **1A, B, C**; the formation of the *cis-syn* isomer **1D** is unlikely for steric reasons. Since only the *trans-anti* isomer of **1** was actually isolable, the macrocyclic complexes **2** and **3** were prepared as models of the *cis*-isomers of **1**. The presence of the tri- and tetramethylene chains in **2** and **3** reduces the number of possible isomeric species in solution. From molecular models, **2** could be expected to be planar, to exist in the *cis-syn* configuration and to be conformationally stable. In the less sterically

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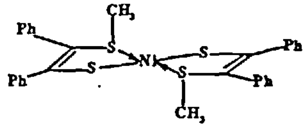
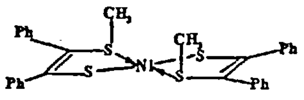
* Author for correspondence.



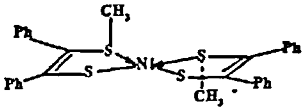
trans-anti-

1A



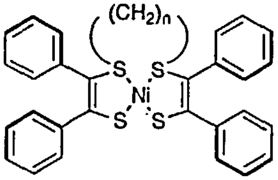
trans-syn-

1B



cis-anti-

1C



n = 3 (2)
4 (3)

constrained **3**, both the *cis-syn-* and the *cis-anti* isomers are possible, however, and the complex should show dynamic properties in solution due to equilibria between the two isomers. Moreover, for **3**, a coordination geometry intermediate between planar and tetrahedral seemed favoured, suggesting that this macrocyclic complex could also serve as a model of the reactive intermediates in the *cis-trans* isomerization reactions of **1** and related dialkyldithiolenes.

EXPERIMENTAL

All common laboratory chemicals were of reagent- or analytical grade. The nickel dithiolene complex, $Ni(S_4C_4Ph_4)$, was synthesized by the method described in reference 6; experiments were performed on a Schlenk line under nitrogen atmosphere where necessary. Room temperature and variable temperature ^1H NMR spectra were recorded on a GE-300 instrument at 300 MHz.

Synthesis of complex 2

Into a Schlenk tube of 250 cm^3 capacity, 3 g (5.6 mmol) of $Ni[S_4C_4Ph_4]$ and 50 cm^3 of methanol were placed and the tube was flushed with nitrogen. To the resulting suspension was added 1.5 cm^3 of 50% sodium hydroxide and 0.20 g of $NaBH_4$. The reaction mixture was then heated to 60°C for 1 hour, and produced a red-brown solution. Under a flow of nitrogen gas, an addition funnel was placed on the Schlenk tube, through which 0.56 cm^3 (5.6 mmol) of 1,3-dibromopropane in 20 cm^3 methanol as added with constant stirring and drop by drop, while the reaction tube was heated in a silicon oil bath to 80°C. Over a period of 4 hours a green-brown precipitate formed which was collected by filtration and recrystallized from CH_2Cl_2/CH_3OH and vacuum-dried, afforded 2.36 g (4.0 mmol) of brown crystals of **2**, mp 260°C, corresponding to 72%, based on $Ni[S_4C_4Ph_4]$. Anal.; calcd. for $C_{31}H_{26}S_4Ni$: C, 63.59; H, 4.47%. Found: C, 63.91; H, 4.32%. Thermolysis mass spectrum [*m/z* (relative intensity, assignment)]: 284 [66, $Ph_2C_2S_2(CH_2)_3$]. 1H NMR (ppm) in $CDCl_3$ at 20°C: 2.95 (t, J = 5 Hz, 4H, $-CH_2-$), 3.03 (q, J = 12 Hz, 2H, $-S-CH_2-$), 6.93–7.25 (m, 20H, Ph).

Synthesis of complex 3

In a similar procedure, 2 g of nickel complex (3.7 mmol) and 0.45 cm^3 of 1,4 dibromobutane (3.7 mmol) were used this time to give crude **3** in the form of a brown-green microcrystalline solid. After recrystallization from CH_2Cl_2/methanol, 1.50 g (2.5 mmol) of brown crystals was obtained, yield, 68%, mp 276°C. Anal.; calcd. for $C_{32}H_{28}S_4Ni$: C, 64.11; H, 4.71%. Found: C, 64.25; H, 4.63%. Thermolysis mass-spectrum, [*m/z* (relative intensity, assignment)] 298 [28.5, $Ph_2C_2S_2(CH_2)_4$]. ^{1}H NMR (ppm) in $CDCl_3$ at 20°C: 2.27 (br s, 4H, -CH_2-), 2.94 (br s, 4H, S-CH_2-), 7.26−6.95 (m, 20H, Ph). For -CH_2-CH_2-S protons, ^{1}H NMR signals at −55° in $CDCl_3$: *cis-anti*-isomer, 1.98 (br s, 4H, -CH_2), 3.09 (br s, 4H, -S-CH_2-); *cis-syn*-isomer, 1.98 (br s, 4H, -CH_2). ^{1}H NMR (ppm in CD_2Cl_2 at −80°C: *cis-anti*-isomer, 1.98 (br s, 4H, -CH_2-), 3.00 (br s, 4H, -S-CH_2-); *cis-syn*-isomer, 2.72 (s, 4H, -CH_2-), 2.69 (s, 4H, -S-CH_2-).

Synthesis of the free ligand thiols

Complex **2**, 1.0 g (1.7 mmol) was placed in a Schlenk tube of 75 cm^3 capacity. After the addition of 10 cm^3 of a saturated aqueous solution of NaCN, and 10 cm^3 of 1.0 M NaOH in methanol, the tube was sealed and heated to 75°C for two hours. After cooling, the tube was opened with care in a vented hood and the reaction solution carefully neutralized with 1 M HCl slowly with strong stirring. The reaction mixture was then transferred to a separating funnel of 500 cm^3 capacity and extracted with 100 cm^3 of diethylether. The yellow ether phase was collected, washed with 3 x 50 cm^3 water, dried with Na_2SO_4 and evaporated to dryness, affording 0.65 g (1.23 mmol) of product as a yellow oil, yield, 72%, based on **2**. Anal.; calcd. for $C_{31}H_{30}S_4$: C, 70.21; H, 5.66%. Found: C, 70.85; H, 5.58%. ^{1}H NMR (ppm) in $CDCl_3$: 1.62 (q, J = 7.2 Hz, 2H, -CH_2-), 2.47 (t, J = 6.9 Hz, 4H, S-CH_2-), 7.05–7.15 (m, 20H, Ph). From 1.0 g (1.67 mmol) of complex **3**, the corresponding free ligand was obtained similarly, yield 0.70 g (1.28 mmol), 74%, based on **3**. Mp, 126°C. Anal.; calcd for $C_{32}H_{32}S_4$: C, 70.60; H, 5.56%. Found: C, 71.12; H, 5.50%. ^{1}H NMR (ppm) in $CDCl_3$: 1.51 (d, J = 5.7 Hz, 4H, -CH_2-), 2.30 (d, J = 5.7 Hz, 4H, S-CH_2-), 7.06–7.12 (m, 20H, Ph).

Synthesis of 2, 3, from the ligands

The free ligand thiols, 0.51 g, each were dissolved in 100 cm^3 of C_2H_5OH. To these solutions, 0.26 g (1 mmol) of $NiCl_2.6H_2O$ was added. Complexes **2** and **3** were formed quantitatively, and were characterized by comparison of the IR- and ^{1}H NMR spectra with the authentic compounds.

X-ray characterization of 2

A brown, acicular single crystal of complex **2**, obtained by recrystallization from CCl_3H-CH_3OH, was put on a glass fibre along the longest dimension and then mounted on a Siemens R3m/V diffractometer for X-ray data collection. The intensities of monitor reflections decreased by approximately 5% during 71 hours of X-ray exposure. An appropriate scale factor was applied to account for the decay. All non-hydrogen atoms except those of $CHCl_3$ were refined anisotropically, the C and Cl atoms of the solvate were refined isotropically. Hydrogen atoms were included in ideal positions with U fixed at 0.08 Å^2. Phenyl rings were treated as regular hexagons of D_{6h} symmetry with C–C = 1.395 Å and C–C–C– = 120°.

A few residual peaks (0.81 eÅ^{-3}) near disordered $CHCl_3$ were present. No absorption correction was applied because of the low value of μ. There was no evidence for secondary extinction. The unit cell dimensions were obtained from 20 reflections in the range of $15 < 2\theta < 30°$. Systematic absences were consistent with space group *Cc* or C2/c (No. 15, $C_{2h}{}^6$). The latter was chosen and later confirmed correct by the successful refinement of the structure.

The nickel atom present in the special position showed four site symmetry from the automatic direct methods routine of the program SHELXTL plus. The positions of the remaining non-hydrogen atoms were determined from a difference Fourier map. Refinements gave final values of R and R_w which are given in Table I. The final difference map had no feature of any chemical significance, though it had a few residual peaks with density of 0.81 eÅ^{-3}. No evidence of secondary extinction was found and no correction was applied.

Positional and thermal parameters, interatomic distances and bond angles, atomic coordinates and equivalent isotropic displacement coefficients, and cell packing diagram are availably as Supplementary Material. Drawings of the complex **2** are shown in Figure 1. Atomic coordinates and a summary of the atomic distances and bond angles are given in Tables II and III.

TABLE I
Crystallographic data collection parameters for complexes 2 and 3.

	2	**3**
Formula	$Ni[(CH_2)_3S_4C_4Ph_4].CHCl_3$	$Ni[(CH_2)_4S_4C_4Ph_4]$
Space group	$C2/c$ (No. 15, C^6_{2h})	$P2_1/n$ (No. 14, C^5_{2h})
a, Å	29.26(2)	10.07(1)
b, Å	8.170(4)	18.22(2)
c, Å	30.76(2)	15.36(2)
β, deg.	116.69(6)	94.56(8)
V, Å^3	6571(8)	2810(5)
T, K	296	296
$d_{calc.}$, g/cm^3	1.425	1.427
Z	8	4
FW	704.8	599.5
λ, Å (MoKα)	0.71073	0.71073
No. of param. refined	309	286
Final R	0.60	0.52
Final R_w	0.68	0.68
R Indices all data	1.10	0.98
R_w (all data)	0.77	0.95
Goodness of fit (S)	2.07	0.94
Largest and mean Δ/σ	0.180, 0.017	0.173, 0.026

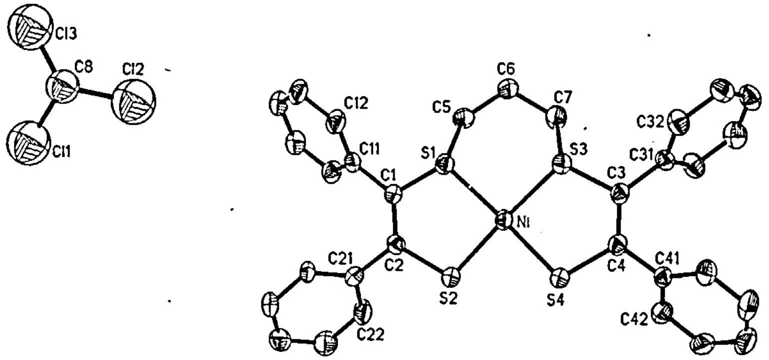


FIGURE 1 Perspective view of the structure of the complex 2 with C and S atoms numbered and with the molecule of $CHCl_3$ present included (the atoms are drawn with 30% probability ellipsoids).

X-ray characterization of 3

The crystal structure of complex 3 was solved similarly to that of 2. The nickel atom of the complex was found from the automatic direct methods routine of the program SHELXTL plus. The position of the remaining non-hydrogenatoms were refined anisotropically, the hydrogen atoms were included in ideal positions with U fixed at $0.08\,Å^2$ and the phenyl rings were treated as outlined above. A residual peak ($0.67\,eÅ^{-3}$) was not connected to any atom or present at any chemically significant position. Absorption corrections were not applied because of the low value of μ. Secondary extinction was not observed. Refinements gave final values of R and R_w which are given in Table I.

Positional and thermal parameters, interatomic distances and bond angles, atomic coordinates and equivalent isotropic displacement coefficients, and cell packing diagrams are available as Supplementary Material. Drawings of the complex 3 are shown in Figure 2. Tables IV and V list atomic coordinates, selected interatomic distances and bond angles for complex 3.

RESULTS AND DISCUSSION

Complexes 2 and 3 were obtained by the reaction of the dianion of bis(cis-stilbenedithiolato)nickel(II) with $Br(CH_2)_3Br$ and $Br(CH_2)_4Br$, respectively. Their constitution was elucidated by degradation studies and independent synthesis from the free ligands $HS(Ph)C{=}C(Ph)\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}C(Ph){=}C(Ph)SH$, 4, 5 ($n=3,4$), X-ray crystallographic structure determinations and 1H NMR spectroscopy (see Experimental section).

Results of variable temperature ^1H NMR measurements are summarized in the Experimental section.

Solid State Structures

In 2, which crystallized with one molecule of solvent ($CHCl_3$), the coordination geometry of nickel is essentially square planar, both with respect to the S–Ni–S bond

TABLE II

Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3), for **2**.

	x/a	*y/b*	*z/c*	U_{eq}*
Ni	3384(1)	2853(2)	528(1)	48(1)
S(1)	2958(1)	2083(3)	916(1)	49(1)
S(2)	3692(1)	4895(3)	1019(1)	58(1)
S(3)	3114(1)	798(3)	25(1)	51(1)
S(4)	3830(1)	3718(3)	171(1)	63(2)
Cl(1)	191(3)	8678(9)	1868(3)	160(3)
Cl(2)	236(3)	6549(10)	1209(3)	170(3)
Cl(3)	−407(3)	6007(11)	1737(3)	166(3)
C(1)	3200(3)	3237(11)	1459(3)	45(5)
C(2)	3495(3)	4561(11)	1475(3)	48(5)
C(3)	3520(3)	748(12)	−264(3)	46(5)
C(4)	3805(4)	2102(12)	−220(3)	51(5)
C(5)	3168(4)	−8(11)	1123(3)	58(5)
C(6)	2998(4)	−1163(12)	697(3)	65(6)
C(7)	3300(4)	−1036(11)	399(3)	66(6)
C(8)	−190(5)	7213(16)	1403(5)	109(4)
C(11)	3060(2)	2703(7)	1848(2)	51(5)
C(12)	2566	2140	1722	62(5)
C(13)	2436	1618	2083	73(6)
C(14)	2798	1659	2570	79(7)
C(15)	3292	2222	2696	69(6)
C(16)	3423	2744	2335	60(5)
C(21)	3649(3)	5879(6)	1851(2)	51(5)
C(22)	4151	6458	2061	73(6)
C(23)	4290	7765	2387	89(7)
C(24)	3927	8493	2503	69(6)
C(25)	3425	7913	2293	59(5)
C(26)	3286	6607	1967	52(5)
C(31)	3500(3)	−757(7)	−543(2)	47(5)
C(32)	3032	−1417	−872	64(6)
C(33)	3019	−2829	−1132	71(6)
C(34)	3474	−3580	−1064	70(6)
C(35)	3943	−2920	−735	72(6)
C(36)	3956	−1508	−475	64(6)
C(41)	4105(3)	2390(7)	−495(2)	51(5)
C(42)	4607	2965	−254	62(5)
C(43)	4881	3299	−515	84(8)
C(44)	4654	3059	−1017	94(9)
C(45)	4153	2485	−1258	84(7)
C(46)	3878	2150	−997	64(5)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor, *i.e.*, $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i . a_j$. Some 7 positions for 3 Cl atoms of the distorted $CHCl_3$ refined with partial occupancy factors. Occupancy factor for Cl(1), Cl(2) or Cl(3) is 65%; that for Cl(1a), Cl(2a) or Cl(2b) is 25%, while that for Cl(3a) is 30%.

TABLE III
Selected geometrical data for *cis-syn*-**2**.*

Distances (Å)			
Ni–S(1)	2.171(4)	Ni–S(2)	2.157(3)
Ni–S(3)	2.176(3)	Ni–S(4)	2.167(4)
S(1)–C(1)	1.765(9)	S(1)–C(5)	1.829(9)
S(2)–C(2)	1.762(12)	S(3)–C(3)	1.778(12)
S(3)–C(7)	1.817)(9)	S(4)–C(4)	1.765(11)
C(1)–C(11)	1.493(13)	C(1)–C(2)	1.370(14)
C(3)–C(4)	1.355(14)	C(2)–C(21)	1.493(11)
C(3)–C(31)	1.485(12)	C(4)–C(41)	1.486(15)
Angles (deg)			
S(1)–Ni–S(2)	90.1(1)	S(1)–Ni–S(3)	93.0(1)
S(2)–Ni–S(3)	176.6(2)	S(1)–Ni–S(4)	176.9(1)
S(2)–Ni–S(4)	86.9(1)	S(3)–Ni–S(4)	90.1(1)
Ni–S(1)–C(1)	106.2(4)	Ni–S(1)–C(5)	106.0(4)
C(1)–S(1)–C(5)	104.0(4)	Ni–S(2)–C(2)	104.8(3)
Ni–S(3)–C(3)	105.2(3)	Ni–S(3)–C(7)	106.1(3)
C(3)–S(3)–C(7)	102.7(5)	Ni–S(4)–C(4)	104.6(4)
S(1)–C(1)–C(2)	115.8(8)	S(1)–C(1)–C(11)	117.6(6)
S(2)–C(2)–C(21)	114.3(7)	S(2)–C(2)–C(1)	121.3(8)
S(3)–C(3)–C(4)	116.8(8)	S(3)–C(3)–C(31)	116.5(7)
C(4)–C(3)–C(31)	126.6(10)	S(4)–C(4)–C(3)	120.9(9)
S(4)–C(4)–C(41)	114.5(7)	C(3)–C(4)–C(41)	124.5(9)
S(1)–C(5)–C(6)	110.9(6)	C(5)–C(6)–C(7)	115.1(9)
S(3)–C(7)–C(6)	110.1(7)		

* Excluding data for the molecule of $CHCl_3$ present.

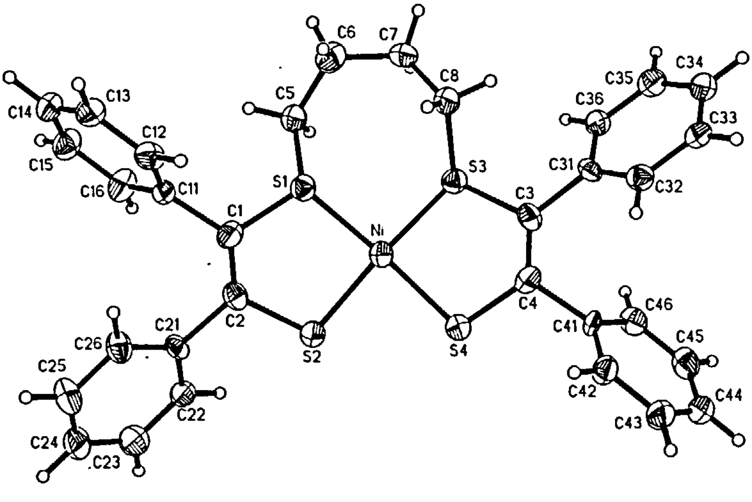


FIGURE 2 Perspective view of the structure of the complex 3 with C and S atoms numbered and hydrogen atoms included (the atoms are drawn with 30% probability ellipsoids).

TABLE IV

Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) for 3.

	x/a	*y/b*	*z/c*	U_{eq}
Ni	1142(1)	1087(1)	4668(1)	44(1)
S(1)	251(2)	1590(1)	5741(1)	45(1)
S(2)	3020(2)	1022(1)	5444(1)	50(1)
S(3)	−674(2)	833(1)	3881(1)	45(1)
S(4)	2239(2)	955(1)	3529(1)	54(1)
C(1)	1461(8)	1536(4)	6651(5)	45(3)
C(2)	2660(9)	1321(4)	6501(5)	43(3)
C(3)	−235(9)	972(4)	2792(5)	50(3)
C(4)	1012(8)	955(4)	2666(5)	45(3)
C(5)	−1201(8)	1113(5)	6124(5)	56(3)
C(6)	−2489(9)	1390(6)	5687(6)	72(4)
C(7)	−2899(8)	1150(5)	4771(5)	57(3)
C(8)	−2072(8)	1449(5)	4054(5)	53(3)
C(11)	946(5)	1816(3)	7490(3)	43(3)
C(12)	434	2527	7502	52(3)
C(13)	−106	2791	8250	63(4)
C(14)	−132	2344	8985	62(4)
C(15)	380	1634	8973	65(4)
C(16)	919	1370	8225	59(3)
C(21)	3868(4)	1332(3)	7141(3)	41(3)
C(22)	4788	760	7134	49(3)
C(23)	5946	778	7696	68(4)
C(24)	6184	1369	8265	74(4)
C(25)	5264	1941	8272	71(4)
C(26)	4106	1922	7710	55(3)
C(31)	−1420(4)	1029(3)	2083(3)	41(3)
C(32)	−1339	1547	1420	50(3)
C(33)	−2370	1609	762	56(3)
C(34)	−3481	1152	766	68(4)
C(35)	−3562	634	1429	60(4)
C(36)	−2531	573	2087	51(3)
C(41)	1552(5)	902(3)	1781(3)	41(3)
C(42)	2442	1436	1535	52(3)
C(43)	3047	1363	754	61(4)
C(44)	2762	755	219	74(4)
C(45)	1872	221	465	67(4)
C(46)	1267	294	1246	56(3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor, *i.e.*, $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i . a_j$.

angles and the planarity of the NiS_4 core (see Figure 1, Table II). The average Ni–S– and Ni–S(CH_2)– bond lengths are 2.162(5) Å and 2.174(4) Å, respectively, the in-plane mean C–S and C–S(CH_2) bonds are 1.763(5) Å and 1.772(10) Å, the S–CH_2– bonds 1.823(9) Å, respectively. The mean ethylenic C=C bond distances are 1.36(1) Å, which compares well with the corresponding distance in the *trans-anti* dimethyl derivative 1A of 1.352(7) Å;[1] the $CHCl_3$ molecule is in a non-interacting position. The

TABLE V
Selected geometrical data for *cis-anti*-3.

Distances (Å)			
Ni-S(1)	2.144(3)	Ni-S(2)	2.157(3)
Ni-S(3)	2.162(3)	Ni-S(4)	2.156(3)
S(1)-C(1)	1.783(8)	S(1)-C(5)	1.837(9)
S(2)-C(2)	1.778(8)	S(3)-C(3)	1.782(9)
S(3)-C(8)	1.837(9)	S(4)-C(4)	1.739(8)
C(1)-C(2)	1.307(12)	C(1)-C(11)	1.515(10)
C(2)-C(21)	1.503(9)	C(3)-C(4)	1.287(12)
C(3)-C(31)	1.554(9)	C(4)-C(41)	1.507(10)
C(5)-C(6)	1.499(12)	C(6)-C(7)	1.501(12)
Angles (deg)			
S(1)-Ni-S(2)	90.0(1)	S(1)-Ni-S(3)	97.7(1)
S(2)-Ni-S(3)	164.4(1)	S(1)-Ni-S(4)	160.8(1)
S(2)-Ni-S(4)	87.6(1)	S(3)-Ni-S(4)	89.3(1)
Ni-S(1)-C(1)	106.1(3)	Ni-S(1)-C(5)	115.9(3)
C(1)-S(1)-C(5)	103.6(4)	Ni-S(2)-C(2)	104.7(3)
Ni-S(3)-C(3)	103.5(3)	Ni-S(3)-C(8)	114.4(3)
C(3)-S(3)-C(8)	107.4(4)	Ni-S(4)-C(4)	103.9(3)
S(1)-C(1)-C(2)	117.4(6)	S(1)-C(1)-C(11)	112.9(5)
S(2)-C(1)-C(11)	129.4(7)	S(2)-C(2)-C(1)	120.8(6)
S(2)-C(2)-C(21)	112.9(5)	C(1)-C(2)-C(21)	126.3(7)
S(3)-C(3)-C(4)	117.1(6)	S(3)-C(3)-C(31)	115.7(6)
C(4)-C(3)-C(31)	126.9(7)	S(4)-C(4)-C(3)	121.9(7)
S(4)-C(4)-C(41)	113.7(5)	C(3)-C(4)-C(41)	124.3(7)
S(1)-C(5)-C(6)	112.3(7)	C(5)-C(6)-C(7)	119.1(8)
C(6)-C(7)-C(8)	116.4(7)	S(3)-C(8)-C(7)	110.7(6)

trimethylene carbon atoms are attached *via* to *syn-cis*-C-S bonds of mean length 1.823(9) Å, the mean Ni-C-S bond angles are 106.2(6) Å.

In complex **3**, see Figure 3, the mean Ni-S and Ni-S(CH_2)- bond lengths are 2.156(5) Å and 2.153(9) Å, respectively, the mean C-S and C-S(CH_2) bonds 1.737(8) Å and 1.765(8) Å, the S-CH_2 bonds 1.832(9) Å, respectively. The ethylenic C=C bonds of 1.30(1) Å (mean) are significantly shorter than in **2**. This is suggestive of an electronically more highly localized structure due to the deviation from planarity of the complex. The coordination geometry is distorted from planar in the direction of the tetrahedron; the mean S-Ni-S(CH_2) bond angles are 89.6(4)° and 162(2)°; the S-Ni-S and CH_2-Ni-S(CH_2) bond angles are 87.6(1)° and 97.7(1)°, respectively. The two S-CH_2- bonds are in the *cis-anti* position; the mean Ni-S-CH_2- angle is 115(1)°. Complexes **2**, **3** resemble to some extent recently described[3] Ni(II) complexes with ligands derived from *N*,*N'*-trimethylene- and *N*,*N'*-tetramethylene bis(methyl-2-amino-1-cyclopentenedithiocarboxylate, **4**, **5**. These complexes show much larger deviations from planarity and are apparently not structurally dynamic in solution. The ligand in **2** also resembles that in the recently reported[4] species Ni(II)-trimethylene-*S*,*S'*-bis(1-thiobenzene-2-thiolate), **6**, Ni[1-$^-$S-C_6H_4-2-$SCH_2CH_2CH_2$-2-SC_6H_4-1-S^-], in which the NiS_4 core is tetrahedrally distorted from planarity. On the other hand, in the cycloaddition product of Ni[$S_4C_4(CF_3)_4$] with 2,3-dimethylbutadiene,[5] 7, the NiS_4 core is planar and the Ni–S– and Ni–S(CH_2–) bond lengths of 2.156(7) and 2.183(8) Å are comparable to the corresponding bonds in **2**, presumably due to the similar steric demands of the 2,3-dimethylbutene- and trimethylene moieties.

Dynamic Behaviour in solution

Variable temperature ^1H NMR studies of **2** in CD_2Cl_2 solution suggest the absence of dynamic behaviour as no changes in the spectra were observed in the temperature range ±50°C. The ^1H NMR spectrum of **3**, however, shows significant changes with temperature. At −55°C in $CDCl_3$, sets of signals of two species predominate. One of them closely resembles that observed in the spectrum of **2** and thus is assigned to the *cis-syn* isomer of **3**, the other is accordingly assigned to the *cis-anti* isomer. No evidence was obtained for the presence of paramagnetic species in solution, thus excluding equilibria between paramagnetic tetrahedral or pseudotetrahedral isomers of **3**, in solutions in the temperature range studied. Such rearrangements may occur at elevated temperatures, however, preceding thermal disproportionation, which is the major pathway of fragmentation on thermolysis.[1]

SUPPLEMENTARY MATERIAL

Equivalent positions, scattering factor tables, least-square parameters, tables of positional parameters, torsion angles and tables of least-square planes, a listing of observed and calculated structure factors and additional perspective drawings of the structures of complexes **2** and **3** (60 pages) can be obtained from GNS.

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