N(5)	0.199 (4)	0.523 (3)	−0.004 (2)	0.06 (1)
N(6)	0.229 (4)	−0.030 (4)	−0.021 (3)	0.10 (1)
C(1)	0.404 (4)	0.293 (5)	0.119 (2)	0.07 (1)
C(2)	0.427 (4)	0.173 (4)	0.145 (3)	0.07 (1)
C(3)	0.334 (5)	0.422 (4)	0.202 (3)	0.05 (1)
C(4)	0.247 (5)	0.456 (4)	0.238 (3)	0.05 (1)
C(5)	0.344 (4)	0.009 (4)	0.202 (2)	0.04 (1)
C(6)	0.244 (5)	−0.021 (4)	0.232 (2)	0.05 (1)
C(7)	0.231 (4)	0.391 (3)	0.093 (2)	0.02 (1)
C(8)	0.283 (5)	0.489 (4)	0.059 (2)	0.05 (1)
C(9)	0.252 (5)	0.067 (4)	0.084 (3)	0.06 (1)
C(10)	0.302 (8)	−0.020 (6)	0.049 (4)	0.14 (2)

Table 2. *Selected geometric parameters (Å, °)*

Pt(1)—N(1)	2.03 (3)	Pt(2)—Cl(3)	2.30 (1)
Pt(1)—N(2)	2.06 (4)	Pt(2)—Cl(4)	2.31 (1)
Pt(1)—N(3)	2.02 (3)	Pt(3)—Cl(5)	2.27 (1)
Pt(1)—N(4)	2.05 (3)	Pt(3)—Cl(6)	2.30 (1)
Pt(2)—Cl(1)	2.32 (1)	Pt(3)—Cl(7)	2.30 (1)
Pt(2)—Cl(2)	2.32 (1)	Pt(3)—Cl(8)	2.31 (1)
N(1)—Pt(1)—N(2)	83 (1)	Cl(2)—Pt(2)—Cl(3)	88.0 (5)
N(1)—Pt(1)—N(3)	86 (1)	Cl(2)—Pt(2)—Cl(4)	179.0 (5)
N(1)—Pt(1)—N(4)	168 (1)	Cl(3)—Pt(2)—Cl(4)	91.0 (5)
N(2)—Pt(1)—N(3)	165 (1)	Cl(5)—Pt(3)—Cl(6)	89.5 (5)
N(2)—Pt(1)—N(4)	85 (1)	Cl(5)—Pt(3)—Cl(7)	176.2 (4)
N(3)—Pt(1)—N(4)	103 (1)	Cl(5)—Pt(3)—Cl(8)	90.2 (5)
Cl(1)—Pt(2)—Cl(2)	92.9 (6)	Cl(6)—Pt(3)—Cl(7)	89.7 (5)
Cl(1)—Pt(2)—Cl(3)	176.7 (5)	Cl(6)—Pt(3)—Cl(8)	174.8 (4)
Cl(1)—Pt(2)—Cl(4)	88.1 (5)	Cl(7)—Pt(3)—Cl(8)	90.9 (5)
Intra- and intermolecular hydrogen-bond contact distances			
Cl(1)···N(3)	3.47 (4)	Cl(3)···N(4)	3.36 (4)
Cl(4)···N(3)	3.43 (4)	Cl(4)···N(4)	3.48 (4)
Cl(6)···N(3)	3.43 (4)	Cl(7)···N(4)	3.44 (4)
Cl(1)···N(5^{i})	3.19 (5)	Cl(1)···N(4^{v})	3.49 (3)
Cl(2)···N(6^{ii})	3.22 (5)	Cl(3)···N(6^{ii})	3.24 (6)
Cl(3)···N(3^{iii})	3.29 (4)	Cl(5)···N(6^{iv})	3.26 (5)
Cl(6)···N(5^{iv})	3.45 (4)	Cl(7)···N(5^{iv})	3.47 (4)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, -z$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Data collection and cell refinement were carried out using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Metal-atom positions were determined by direct methods (*SAPI90*; Fan, 1990). The remaining non-H atoms were located using the *DIRDIF* program (Parthasarathi, Beurskens & Slot, 1993) and were refined anisotropically by full-matrix least squares. Pt, Cl and O atoms were treated anisotropically, and N and C atoms were treated isotropically. H atoms of the penten ligand were located in their calculated positions (C—H 0.95, N—H 0.87 Å) and were not refined. H atoms of water molecules were not located. Relatively large positive and negative peaks were found in the final difference Fourier map but these were all error peaks located near the Pt and Cl atoms. Best-plane calculations were performed with the *BP70* program developed by Ito (1982). All other calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 543–545

Nickel(II) Bis(*d*-campholyl-*l*-campholylmethanate)

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Abstract

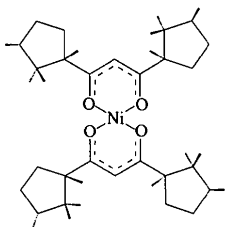
The title compound, bis{1-[(+)-(1*R*,3*S*)-1,2,2,3-tetramethylcyclopentyl]-3-[(−)-(1*S*,3*R*)-1,2,2,3-tetramethylcyclopentyl]propane-1,3-dionato-*O*,*O*′}nickel(II), [Ni($C_{21}H_{35}O_2$)$_2$], displays interesting stereochemical aspects due to the *meso* configuration of the 1,3-bis(1,2,2,3-tetramethylcyclopentyl)-1,3-propanedionate ligands. The Ni atom lies on an inversion centre, with Ni—O distances of 1.842 (2) and 1.826 (2) Å.

Comment

Chiral metal β-diketonates, *e.g.* europium(III) tris[3-heptafluorobutanoyl-(1*R*)-camphorate] or nickel(II) bis-[3-heptafluorobutanoyl-(1*R*)-camphorate], are important auxiliaries for the discrimination of enantiomers in

NMR spectroscopy (Goering, Eikenberry, Koerner & Lattimer, 1974) and gas chromatography (Schurig & Buerkle, 1982).

Europium(III) tris(*d*,*d*-dicampholylmethanate) is employed as a versatile paramagnetic shift reagent for the determination of enantiomeric purities by NMR (McCreary, Lewis, Wernick & Whitesides, 1974). Homochiral nickel(II) bis(*d*,*d*-dicampholylmethanate), as well as the heterochiral nickel(II) bis(*d*-campholyl-*l*-campholylmethanate), (I), have also been prepared (Ossig, 1990). In the *meso* complex, with a square-planar coordination sphere, the heterochiral bis(campholyl)methanate ligands may be related by *cis* or *trans* geometry. This rare case of *cis*/*trans* isomerism is governed exclusively by the chirality of the cyclopentyl groups.



(I)

In the title compound (Fig. 1), the *trans* arrangement is observed, with the Ni site on an inversion centre. Thus, only one of the two possible diastereomers of the title compound is found in the solid state.

The bond lengths and angles in the compound lie within the expected ranges. The bite angle O1—Ni—O2 of the chelating dicampholyl ligand is 94.8 (1)°. The resulting metallacycle (Ni, O1, C1, C2, C3, O2) exhibits no significant deviations from planarity. The cyclopentane rings, C4–C8 and C13–C17, are both found to have envelope conformations (Cremer & Pople, 1975), with atom C5 0.63 (1) Å from the plane of C4, C6, C7 and C8, and atom C14 0.61 (1) Å from the plane of C13, C15, C16 and C17.

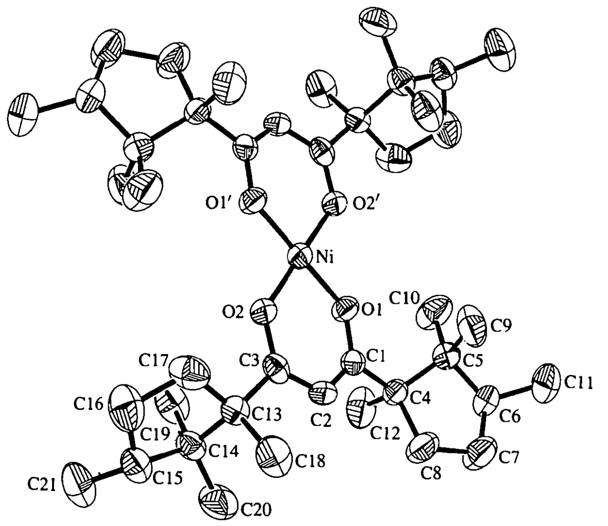


Fig. 1. The molecular structure of the title compound showing 50% probability ellipsoids.

Experimental

The title compound was prepared by reaction of ethanolic solutions of the Na salt of *d*,*l*-dicampholylmethane and $NiCl_2.6H_2O$. After 24 h stirring, the solution was filtered and the residue dissolved in *n*-hexane. Violet needles crystallized from this solution in a chamber having an ethanol atmosphere.

Crystal data

$[Ni(C_{21}H_{35}O_2)_2]$
$M_r = 697.69$
Triclinic
$P\overline{1}$
$a = 7.3319 (8)$ Å
$b = 12.3885 (9)$ Å
$c = 12.8313 (9)$ Å
$\alpha = 114.805 (9)°$
$\beta = 98.699 (9)°$
$\gamma = 100.923 (9)°$
$V = 1003.37 (2)$ Å^3
$Z = 1$
$D_x = 1.155$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 16–38°$
$\mu = 0.948$ mm^{-1}
$T = 293 (2)$ K
Needle
0.40 × 0.15 × 0.10 mm
Violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.45$, $T_{\max} = 1.00$
3715 measured reflections
3419 independent reflections

1432 observed reflections $[F > 4\sigma(F)]$
$R_{\rm int} = 0.016$ (F)
$\theta_{\max} = 65°$
$h = 0 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0446$
$wR(F^2) = 0.1204$
$S = 1.119$
1432 reflections
227 parameters
H(2) refined freely, other H atoms refined as riding model (*SHELXL*93; Sheldrick, 1993)
$w = 1/[\sigma^2(F_o^2) + (0.1130P)^2 + 1.6245P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.395$ e Å^{-3}
$\Delta\rho_{\min} = -0.274$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.012 (1)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	1/2	1/2	1/2	0.0373 (5)
O1	0.3951 (3)	0.6259 (2)	0.5068 (2)	0.0419 (8)
O2	0.5421 (3)	0.5471 (2)	0.6589 (2)	0.0402 (7)

C1	0.3427 (5)	0.6974 (3)	0.5951 (4)	0.038 (1)
C2	0.3809 (6)	0.7011 (4)	0.7051 (4)	0.043 (1)
C3	0.4874 (5)	0.6316 (4)	0.7353 (3)	0.039 (1)
C4	0.2441 (5)	0.7863 (3)	0.5709 (3)	0.040 (1)
C5	0.1012 (5)	0.7275 (3)	0.4461 (3)	0.044 (1)
C6	−0.0192 (5)	0.8208 (4)	0.4629 (3)	0.049 (1)
C7	−0.0451 (7)	0.8595 (5)	0.5870 (4)	0.078 (2)
C8	0.1152 (7)	0.8328 (5)	0.6549 (4)	0.073 (2)
C13	0.5498 (5)	0.6567 (3)	0.8646 (3)	0.039 (1)
C14	0.7248 (5)	0.7765 (3)	0.9368 (3)	0.045 (1)
C15	0.8144 (6)	0.7581 (4)	1.0417 (3)	0.054 (1)
C16	0.7977 (7)	0.6206 (4)	0.9889 (4)	0.078 (2)
C17	0.6327 (7)	0.5557 (4)	0.8772 (4)	0.064 (1)
C12	0.4111 (6)	0.8963 (4)	0.5922 (5)	0.079 (2)
C10	0.1978 (8)	0.7147 (5)	0.3452 (4)	0.084 (2)
C9	−0.0245 (6)	0.6006 (4)	0.4171 (4)	0.077 (2)
C11	−0.2090 (6)	0.7755 (5)	0.3683 (4)	0.076 (1)
C18	0.3771 (6)	0.6646 (5)	0.9194 (4)	0.068 (1)
C20	0.6677 (7)	0.8982 (4)	0.9813 (4)	0.080 (2)
C19	0.8642 (6)	0.7803 (4)	0.8607 (4)	0.068 (1)
C21	1.0186 (6)	0.8405 (5)	1.1136 (4)	0.081 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ni—O2	1.826 (2)	O2—C3	1.279 (4)
Ni—O1	1.842 (2)	C1—C2	1.375 (5)
O1—C1	1.279 (4)	C2—C3	1.395 (6)
Other C—C bond lengths in the range 1.518 (6)–1.572 (5) Å			
O2—Ni—O1	94.8 (1)	C2—C1—C4	122.1 (4)
C1—O1—Ni	125.9 (2)	C1—C2—C3	124.4 (4)
C3—O2—Ni	127.2 (2)	O2—C3—C2	122.7 (4)
O1—C1—C2	123.8 (4)	O2—C3—C13	116.6 (3)
O1—C1—C4	114.1 (3)	C2—C3—C13	120.6 (4)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADHKL4* in *CADSHEL* (Kopf & Ruebcke, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 545–548

$[Re(NNPh)(NNHPh)\{2\text{-}S\text{-}C_5H_3N\text{-}3\text{-}Si(CH_3)_3\}(PPh_3)_2]BPh_4$

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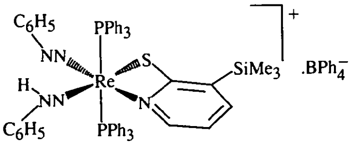
Abstract

We report the crystal structure of (phenyldiazenido-*N*)[phenylhydrazido(2−)-*N*][3-(trimethylsilyl)-2-pyridinethiolato-*S*,*N*]bis(triphenylphosphine-*P*)rhenium tetraphenylborate, $[Re(C_6H_5N_2)(C_6H_6N_2)(C_8H_{12}NSSi)(C_{18}H_{15}P)_2](C_{24}H_{20}B)$, prepared by the reaction of $[ReCl(C_6H_6N_2)_2(C_{18}H_{15}P)_2]$ with 3-(trimethylsilyl)-2-pyridinethiol in ethanol. The mixed diazenide/hydrazido(2−) complex represents a relatively rare class of complex.

Comment

The chemistry of hydrazido(2−) complexes has been of great interest since they were identified as intermediates in the protonation of coordinated dinitrogen to ammonia (Chatt, Pearman & Richards, 1975, 1977). As part of a continuing program aimed at defining structural parameters and the chemical reactivity of hydrazido(2−) ligands, we have previously synthesized a number of Mo and W (Chatt, Crichton, Dilworth, Dahlstrom, Gutkoska & Zubieta, 1982; Bishop, Chatt, Dilworth, Hursthouse & Motevalli, 1979; Bishop, Butler, Chatt, Dilworth & Leigh, 1979; Dilworth, Harrison, Walton & Schweda, 1985), Re (Dilworth, Jobanputra, Parrott, Thompson, Povey & Zubieta, 1992) and Tc (Archer, Dilworth, Jobanputra, Thompson, McPartlin, Povey, Smith & Kelly, 1990) hydrazide complexes, with a wide range of coligands. The title complex, (1), can be compared to the only other examples of this type, $[M\mathrm{Br}_2(NNPh)(NNHPh)(PPh_3)_2]$ (M = Tc, Re), which were prepared by protonation of the parent



(1)

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