

Bis{*N*-[3-(4-chlorophenylimino)-2-phenyl-1-propenyl]-4-chloroanilinato-*N,N'*} nickel(II)

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**Abstract.**  $C_{42}H_{30}Cl_4N_4Ni$ ,  $Ni(C_{21}H_{15}Cl_2N_2)_2$ , monoclinic,  $C2/c$ ,  $a = 10.103$  (3),  $b = 19.574$  (5),  $c = 18.937$  (5) Å,  $\beta = 96.24$  (2)°,  $M_r = 791.3$ ,  $Z = 4$ ,  $D_x = 1.41$  Mg m<sup>-3</sup>. The molecule contains a crystallographic  $C_2$  axis. The coordination at Ni is pseudotetrahedral with average Ni–N = 1.945 (2) Å. Considerable deviations from an idealized tetrahedral geometry around Ni occur through both stretching and diagonal twisting of the  $N_4$  tetrahedron.

**Introduction.** Cell dimensions were determined by a least-squares fit to settings for 15 reflexions  $\pm(hkl)$  on a Syntex  $P2_1$  diffractometer (Cu  $K\alpha$  radiation,  $\lambda = 1.54178$  Å). Data collection was carried out in the  $\theta$ – $2\theta$  mode ( $3 < 2\theta < 135^\circ$ ) with graphite-monochromated Cu  $K\alpha$  radiation. A numerical absorption correction was applied. After application of the observation criterion  $F > 3.0\sigma(F)$ , 2889 unique reflexions were retained for use in the structure analysis. The structure was solved by Patterson and difference syntheses and refined by a blocked full-matrix least-squares procedure with anisotropic temperature factors for the non-hydrogen atoms. The H atom positional parameters were refined freely with individual isotropic temperature factors. The terminal value of  $R_w$  was 0.057 with  $R = 0.053$ . The weights were  $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$  where  $g$  refined to 0.000629. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Table 1 lists the final non-hydrogen atom coordinates, Table 2 the bond lengths and angles.†

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† Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34066 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The very small electronic perturbation represented by the transmission of unpaired spin density from a Ni atom into an organic ligand has been shown to provide a powerful tool for conformational analysis (Knorr, Polzer & Bischler, 1975). Thus the apparent interplanar angle of the C(3) phenyl substituent ( $R^3 = Ph$ ) in pseudotetrahedral Ni complexes of type (1) may be inferred from the paramagnetically induced <sup>1</sup>H NMR shifts (Knorr, Weiss, Polzer & Bischler, 1975).

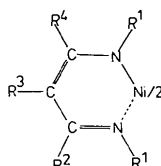
Table 1. Positional parameters ( $\times 10^4$ ) for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	0	1203 (1)	2500
N(1)	826 (2)	1884 (1)	1940 (1)
C(2)	698 (3)	2562 (1)	2008 (1)
C(3)	0	2895 (2)	2500
N(4)	–755 (2)	518 (1)	1832 (1)
C(5)	–642 (3)	–155 (1)	1911 (1)
C(6)	0	–493 (2)	2500
C(11)	1468 (3)	1655 (1)	1353 (1)
C(12)	1201 (3)	1935 (2)	680 (2)
C(13)	1846 (4)	1694 (2)	120 (2)
C(14)	2751 (3)	1173 (2)	234 (2)
C(15)	3010 (4)	878 (2)	887 (2)
C(16)	2361 (3)	1115 (2)	1451 (2)
Cl(14)	3575 (1)	891 (1)	–472 (1)
C(31)	0	3660 (2)	2500
C(32)	–1110 (3)	4023 (1)	2642 (2)
C(33)	–1095 (3)	4731 (2)	2660 (2)
C(34)	0	5085 (2)	2500
C(41)	–1393 (3)	762 (1)	1171 (1)
C(42)	–1169 (4)	476 (2)	530 (2)
C(43)	–1749 (4)	743 (2)	–106 (2)
C(44)	–2567 (3)	1302 (2)	–97 (2)
C(45)	–2790 (4)	1596 (2)	529 (2)
C(46)	–2224 (3)	1328 (2)	1165 (2)
Cl(44)	–3260 (1)	1644 (1)	–901 (1)
C(61)	0	–1256 (2)	2500
C(62)	72 (4)	–1622 (2)	1880 (2)
C(63)	55 (6)	–2335 (2)	1881 (3)
C(64)	0	–2683 (3)	2500

Table 2. Bond lengths (Å) and angles (°)

N(1)—Ni	1.947 (2)	N(4)—Ni	1.943 (2)
C(2)—N(1)	1.341 (3)	C(11)—N(1)	1.419 (4)
C(3)—C(2)	1.390 (3)	C(31)—C(3)	1.498 (5)
C(5)—N(4)	1.331 (3)	C(41)—N(4)	1.426 (3)
C(6)—C(5)	1.395 (3)	C(61)—C(6)	1.493 (5)
C(12)—C(11)	1.386 (4)	C(16)—C(11)	1.388 (4)
C(13)—C(12)	1.388 (5)	C(14)—C(13)	1.370 (5)
C(15)—C(14)	1.364 (5)	Cl(14)—C(14)	1.742 (4)
C(16)—C(15)	1.392 (5)	C(32)—C(31)	1.379 (3)
C(33)—C(32)	1.387 (4)	C(34)—C(33)	1.367 (4)
C(42)—C(41)	1.378 (4)	C(46)—C(41)	1.390 (4)
C(43)—C(42)	1.386 (4)	C(44)—C(43)	1.371 (5)
C(45)—C(44)	1.360 (5)	Cl(44)—C(44)	1.739 (3)
C(46)—C(45)	1.379 (5)	C(62)—C(61)	1.384 (4)
C(63)—C(62)	1.396 (5)	C(64)—C(63)	1.362 (6)
N(4)—Ni—N(1)	106.2 (1)	C(2)—N(1)—Ni	125.0 (2)
C(11)—N(1)—Ni	118.0 (2)	C(11)—N(1)—C(2)	116.5 (2)
N(1)—Ni—N(1)	93.6 (1)	C(3)—C(2)—N(1)	126.1 (2)
C(2)—C(3)—C(2)	124.1 (3)	C(31)—C(3)—C(2)	118.0 (2)
C(5)—N(4)—Ni	126.0 (2)	C(41)—N(4)—Ni	116.6 (2)
C(41)—N(4)—C(5)	117.2 (2)	N(4)—Ni—N(4)	92.7 (1)
C(6)—C(5)—N(4)	126.0 (2)	C(5)—C(6)—C(5)	123.3 (3)
C(61)—C(6)—C(5)	118.3 (2)	C(12)—C(11)—N(1)	122.3 (2)
C(16)—C(11)—N(1)	118.8 (2)	C(16)—C(11)—C(12)	118.9 (3)
C(13)—C(12)—C(11)	120.5 (3)	C(14)—C(13)—C(12)	119.5 (3)
C(15)—C(14)—C(13)	121.2 (3)	Cl(14)—C(14)—C(13)	118.7 (3)
Cl(14)—C(14)—C(15)	120.1 (3)	C(16)—C(15)—C(14)	119.6 (3)
C(15)—C(16)—C(11)	120.3 (3)	C(32)—C(31)—C(3)	121.0 (2)
C(33)—C(32)—C(31)	120.8 (3)	C(32)—C(31)—C(32)	118.0 (3)
C(34)—C(33)—C(32)	120.5 (3)	C(33)—C(34)—C(33)	119.2 (4)
C(42)—C(41)—N(4)	122.3 (2)	C(46)—C(41)—N(4)	119.4 (2)
C(46)—C(41)—C(42)	118.3 (3)	C(43)—C(42)—C(41)	121.2 (3)
C(44)—C(43)—C(42)	119.3 (3)	C(45)—C(44)—C(43)	120.3 (3)
Cl(44)—C(44)—C(43)	118.8 (3)	Cl(44)—C(44)—C(45)	120.8 (3)
C(46)—C(45)—C(44)	120.6 (4)	C(45)—C(46)—C(41)	120.2 (3)
C(62)—C(61)—C(6)	121.2 (2)	C(63)—C(62)—C(61)	121.0 (4)
C(62)—C(61)—C(62)	117.7 (4)	C(64)—C(63)—C(62)	120.1 (4)
C(63)—C(64)—C(63)	120.1 (6)		

It was also demonstrated that asymmetrically substituted complexes of type (1) with  $R^2 \neq R^4$  may be chiral and configurationally stable on the NMR time scale (Knorr, Weiss, Polzer & Raple, 1977). We report here the X-ray structure of the title compound (2), which represents the first such study of a pseudotetrahedral bis-chelate with N<sub>4</sub> coordination and provides conformational data for (2) in the crystalline state.



(1)

(2):  $R^1 = p\text{-Cl-C}_6\text{H}_5$   
 $R^2 = R^4 = \text{H}$   
 $R^3 = \text{C}_6\text{H}_5$

A perspective view of a molecule of the title compound is shown in Fig. 1. The molecules display a crystallographic C<sub>2</sub> axis. The observed severe distortions

from a perfect T<sub>d</sub> symmetry about Ni are of a twofold nature. Like many other pseudotetrahedral chelate complexes, (2) is elongated along its primary C<sub>2</sub> axis bisecting the endocyclic N—Ni—N angles. The extent of this stretching of the N<sub>4</sub> tetrahedron may be gauged by a comparison of the endocyclic chelate angles of 93.6 (1) and 92.7 (1)° with that of 106.2 (1)° for the exocyclic N(1)—Ni—N(4) angle. This provides independent evidence to settle a long-standing controversy bearing on the 3d-orbital sequence (Lin & Orgel, 1964; Eaton & Phillips, 1965), at least for its geometrical supposition in (2). Secondly, the diagonal-twist distortion of the N<sub>4</sub> tetrahedron is 21.5° from an orthogonal D<sub>2d</sub> arrangement of the chelate moieties and is associated with a widening of the exocyclic N(1)—Ni—N(4) angle to 131.8 (1)°. Such pseudotetrahedral flattening along the secondary molecular C<sub>2</sub> axis (bisecting the aforementioned exocyclic angles) may be compared to similar estimates from theoretical calculations (Eliañ & Hoffmann, 1975). An alternative description of the distortion from T<sub>d</sub> symmetry may be sought in the dihedral angles formed by the normals to adjacent polytopal faces (Muetterties & Guggenberger, 1974). For a perfect N<sub>4</sub> tetrahedron all six dihedral angles are 109.5°. With the nomenclature of Muetterties & Guggenberger for (2), δa<sub>3</sub> and δa<sub>5</sub> are 84.2° [edges N(1)···N(4) and N(1)···N(4)], δa<sub>1</sub> and δa<sub>6</sub> are 127.9 and 127.5° [edges N(1)···N(1) and N(4)···N(4)] and δa<sub>2</sub> and δa<sub>4</sub> are 119.4° [edges N(1)···N(4) and N(1)···N(4)]. The difference between the latter dihedral-angle pairs is a measure of the elongation of the N<sub>4</sub> tetrahedron.

Only very small deviations from planarity are found for the chelate rings. Distances from the least-squares plane through Ni, N(1), C(2) and C(3) are Ni —0.003, N(1) 0.008, C(2) —0.010, C(3) 0.004 Å and from that through Ni, N(4), C(5) and C(6), Ni —0.003, N(4) 0.009, C(5) —0.010, C(6) 0.004 Å. Reflecting the decreased strength of the Ni—N σ-bond in tetrahedral as opposed to square-planar complexes, the average Ni—N distance of 1.945 (2) Å in (2) is 0.08 Å longer

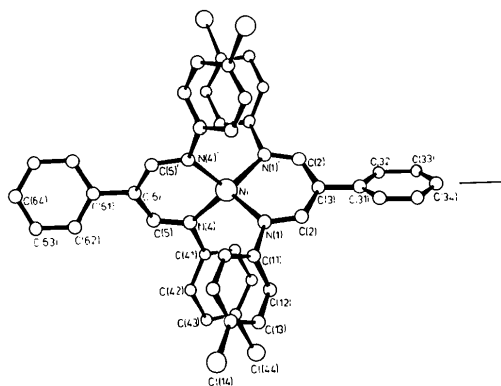


Fig. 1. The molecule (2) in perspective with the numbering scheme.

than that in the planar chelate N<sub>4</sub> complex bis(3-methyl-1-phenyl-5-*p*-tolylformazyl)nickel(II) (Dale, 1967) or in the macrocyclic N<sub>4</sub>-coordinated Ni complex related to (1) by R<sup>1</sup>R<sup>1</sup>-bridging (Hanić, Handlović & Lindgren, 1972). It is also 0.025 Å longer than the Ni—N distance in the planar chelate O<sub>2</sub>N<sub>2</sub> complex bis(*N*-isopropyl-3-methylsalicylaldiminato)nickel(II) (Braun & Lingafelter, 1966) but shorter than those of 1.970 and 1.974 Å in the pseudotetrahedral chelate O<sub>2</sub>N<sub>2</sub> complexes bis(*N*-isopropylsalicylaldiminato)nickel(II) (Fox, Orioli, Lingafelter & Sacconi, 1964) and bis(*N*-isopropyl-3-ethylsalicylaldiminato)nickel(II) (Braun & Lingafelter, 1967). The chelate ring systems are symmetrical with average C—N and C—C distances of 1.336 and 1.392 Å. They are inclined to one another at 67.7° and make respective interplanar angles of 46.6 and 42.5° with their *p*-chlorophenyl and 34.4 and 35.4° with their phenyl substituents. The thermal motions of the phenyl substituents on C(3) and C(6) are more pronounced than those on N(1) and N(4), thereby correlating with NMR evidence for thermally excited rotation of the former phenyl rings on the basis of the temperature dependence of their <sup>1</sup>H NMR shifts (Knorr, Weiss, Polzer & Bischler, 1975). An important stabilizing factor favouring the tetrahedral ground state must be the interaction between the phenyl rings on N(1) and N(4). These make an interplanar angle of 16.5° to one another at a distance between their plane normals of 4.07 Å. Seven of the constituent C atoms are at intermolecular distances of less than 4.0 Å from

members of the other phenyl group. Nevertheless, rotation of such phenyl groups in (2) is fast in solution on the NMR time scale.

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## Dicarbonyl( $\eta$ -triphenylphosphoniumcyclopentadienylide)cobalt(I) Tetracarbonylcobaltate(–I)

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**Abstract.** [Co(C<sub>23</sub>H<sub>19</sub>P)(CO)<sub>2</sub>][Co(CO)<sub>4</sub>], C<sub>29</sub>H<sub>19</sub>Co<sub>2</sub>O<sub>6</sub>P, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 9.777 (2), *b* = 16.797 (6), *c* = 16.799 (5) Å,  $\beta$  = 96.11 (2)°, *Z* = 4, *M<sub>r</sub>* = 611.80, *D<sub>x</sub>* = 1.48 Mg m<sup>-3</sup>, *R* = [ $\sum w|\Delta F|^2 / \sum wF_o^2$ ]<sup>1/2</sup> = 0.0535 based on 3155 independent reflections. The structure consists of two  $\sigma$ -bonded carbonyl groups and the cyclopentadienylide moiety  $\pi$ -bonded to the cobalt(I) to form the cation with square-

planar coordination [the carbonyl—Co—carbonyl bond angle in the cation is 94.5 (3)°] and a tetrahedral [Co(CO)<sub>4</sub>]<sup>-</sup> anion.

**Introduction.** Intensity data (15706 total reflections, 4823 independent reflections, 3155 with intensities greater than three standard deviations above background) were collected to  $\sin \theta/\lambda = 0.6 \text{ \AA}^{-1}$  using a