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assisted with collection of the diffraction data.

Registry No. $(Me_4N)_2[(\mu\text{-}SPh)_6(ZhSPh)_2(ZnCl)_2]$, 76900-55-5; $(Me_4N)_2[(\mu\text{-}SPh)_6(ZnSPh)_2(ZnBr)_2]$, 76915-19-0; $(Me_4N)_2[(\mu\text{-}SPh)_6(ZnSPh)_3(ZnCl)]$, 76900-57-7; $(Me_4N)_2[Zn_4(SPh)_{10}]$, 76915-21-4; $(Me_4N)_2[Zn(SPh)_4]$, 76915-22-5.

Supplementary Material Available: A complete tabulation of the atomic parameters and a listing of F_o and F_c (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Inorganic Chemistry, Charles University, 12840 Prague, Czechoslovakia

Crystal Structure of a Nickel(II) Complex of a Chiral Bis(tertiary phosphine), Bromo[(*R*,*S*)-3,6-diphenyl-3,6-diphosphaoctanedioato(1−)][(*S*,*R*)-3,6-diphenyl-3,6-diphosphaoctanedioic acid]nickel(II) Hydrate

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The complex $[NiBr(HQ)(H_2Q)]\cdot H_2O$ containing the chiral bis(tertiary phosphine), $HO_2CCH_2(C_6H_5)PCH_2CH_2P(C_6H_5)CH_2CO_2H$ (H_2Q) was studied by single-crystal X-ray structural analysis. The crystal is monoclinic, $P2_1/c$, with a = 12.155 (2) Å, b = 18.286 (3) Å, c = 17.336 (4) Å, β = 102.41 (1)°, and Z = 4. The structure was determined from 3065 reflections measured on a Syntex $P2_1$ diffractometer and solved and refined by conventional Patterson, Fourier, and least-squares techniques to R = 0.046 and R_w = 0.058. All atoms except four disordered methylene hydrogens were located. The central nickel atom is five-coordinated by four phosphorus atoms forming a basal plane and bromide at the top of a tetragonal pyramid. Carboxyl groups and the water molecule are not coordinated to nickel. The stereochemistry of the complex with respect to the chiral phosphorus atoms corresponds to the anti-bis(meso-ligand) configuration. The two phosphine ligands are not equivalent: one of the chelate rings suffers from disorder of the methylene groups while the second adopts a normal λ-skew conformation. The other difference between the ligands as follows from electroneutrality demands, i.e., one being HQ^- and the other H_2Q, is rather formal because of extensive hydrogen bonding that counterbalances the differences between the carboxyls and constitutes a three-dimensional network holding the structure together.

Introduction

Complexes of chiral bis(tertiary phosphines) attract considerable interest because of their application in stereospecific homogeneous catalysis. Among many phosphine ligands, those functionalized by a second, typically hard donor group are described only rarely[2-7] despite the obvious fact that such "hybrid" ligands could exhibit properties differing significantly from those of simple phosphines. As discussed recently by Meek and co-workers,[7] the solubility of complexes, the affinity toward hard metal ions, and, hence, the catalytic activity can be expected to be influenced by the second, hard donor. A series of ligands of this type, $(C_6H_5)_{3-n}P(CH_2CO_2H)_n$ (n = 1–3), was synthesized in this laboratory[8-10] and has been proved to coordinate selectively to various metal ions. An extension of this series includes a chiral bis(tertiary phosphine) of the "hybrid" type, namely, 3,6-diphenyl-3,6-diphosphaoctanedioic acid (hereafter, H_2Q), $HO_2CCH_2(C_6H_5)PCH_2CH_2P(C_6H_5)CH_2CO_2H$, which was synthesized in small yields,[11] presumably mainly because of the isolation from a mixture of diastereoisomers. The more efficient synthesis of the same diastereoisomer (as indicated by the melting point) was described independently.[12] As the indentification of the isolated diastereoisomer by the X-ray structure determination suffered from imperfectness of the H_2Q crystals, a derivative which would crystallize well was sought to serve for this purpose. Nickel complexes synthesized and characterized previously[13] are the obvious candidates as they are prepared under mild conditions where the configuration of the ligand can safely be expected to remain unchanged.

Experimental Section

The title complex was synthesized by mixing 0.19 g of $H_2Q\cdot 0.25(dioxane)$[11] (0.5 mmol) dissolved in 5 mL of acetic acid with 0.25 mmol of $NiBr_2$ dissolved in 1 mL of water and allowing water vapor to diffuse into the solution in a closed vessel. With gradual decrease of the acetic acid concentration to ca. 30%, orange single crystals grew during several days at room temperature, yielding ca. 90% of the theoretical amount. Together with the homogeneity of the material (as proved by mp and TLC), this yield confirms that the original sample of H_2Q was not a mixture of diastereoisomers.

The IR spectrum (Nujol and Fluorolube mulls) indicated protonized and dissociated carboxyl groups in approximately a 3:1 ratio, as well as the presence of water (two small $\nu(H_2O)$ bands at 3500 and 3565 cm^{-1}). In accordance with further analytical data, the complex is best formulated as $[NiBr(HQ)(H_2Q)]\cdot H_2O$. Anal. Calcd for $C_{36}H_{41}BrNiO_9P_4$: Ni, 6.67; Br, 9.08; P, 14.07; H_2O, 2.05. Found: Ni, 6.73; Br, 9.14; P, 13.98; H_2O, 2.1 (weight loss at 170 °C under argon). The product is not identical with that obtained from aqueous acetone.[13]

Solution and Refinement of the Structure

A crystal of the title compound (dimensions 0.3 × 0.3 × 0.1 mm^3) was placed on a goniometer head in a general position. The crystal was found to be monoclinic with a = 12.155 (2) Å, b = 18.286 (3) Å, c = 17.336 (4) Å, β = 102.41 (1)°, and V = 3763 (1) $Å^3$. The cell dimensions were obtained by the least-squares fit of 17 reflections in the range $20° \le 2\theta \le 25°$, measured on a Syntex $P2_1$ automated diffractometer at room temperature with use of graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Systematic absences

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Table I. Final Atomic Coordinates (×10⁴; for H, ×10³) and Their Esd's and Isotropic Temperature Factors (Å²) for Disordered Carbons and for Hydrogen Atoms

atom	x	y	z	B
Ni	1251.9 (7)	1571.8 (4)	2195.6 (5)	
Br	1219.4 (6)	1034.3 (4)	810.8 (4)	
P(1)	−128 (1)	836 (1)	2377 (1)	
P(2)	2346 (1)	820 (1)	3049 (1)	
P(3)	2634 (1)	2372 (1)	2181 (1)	
P(4)	66 (1)	2476 (1)	1765 (1)	
C(11)	−540 (6)	1015 (4)	3316 (4)	
C(12)	−1250 (5)	421 (4)	3608 (4)	
O(1A)	−1541 (4)	−124 (2)	3222 (3)	
O(1B)	−1520 (4)	570 (3)	4263 (3)	
C(21)	2710 (7)	1192 (4)	4060 (4)	
C(22)	2769 (6)	611 (4)	4683 (4)	
O(2A)	3569 (4)	227 (3)	4913 (3)	
O(2B)	1839 (4)	593 (3)	4960 (3)	
C(31)	3513 (8)	2097 (5)	1498 (5)	
C(32)	4418 (7)	2622 (5)	1371 (5)	
O(3A)	5400 (5)	2463 (3)	1581 (3)	
O(3B)	4065 (5)	3220 (4)	998 (4)	
C(41)	−976 (7)	2322 (4)	849 (4)	
C(42)	−1436 (6)	3000 (4)	395 (4)	
O(4A)	−2310 (5)	3263 (4)	452 (4)	
O(4B)	−839 (5)	3254 (3)	−57 (3)	
O(5)	5715 (6)	3896 (4)	644 (5)	
C(13)	−1452 (5)	729 (3)	1656 (4)	
C(14)	−2446 (6)	1029 (4)	1769 (5)	
C(15)	−3436 (6)	939 (4)	1218 (5)	
C(16)	−3447 (7)	528 (5)	550 (5)	
C(17)	−2461 (7)	235 (5)	432 (5)	
C(18)	−1454 (6)	326 (4)	977 (4)	
C(23)	3642 (5)	460 (4)	2826 (4)	
C(24)	4680 (6)	492 (5)	3355 (5)	
C(25)	5613 (7)	159 (5)	3154 (5)	
C(26)	5524 (7)	−192 (5)	2450 (5)	
C(27)	4486 (7)	−227 (5)	1922 (5)	
C(28)	3551 (6)	102 (4)	2112 (5)	
C(33)	3644 (7)	2599 (4)	3086 (4)	
C(34)	4712 (7)	2294 (5)	3254 (5)	
C(35)	5471 (10)	2411 (8)	3959 (6)	
C(36)	5161 (14)	2839 (8)	4483 (8)	
C(37)	4165 (14)	3192 (7)	4384 (7)	
C(38)	3382 (10)	3059 (5)	3657 (7)	
C(43)	−707 (6)	2830 (3)	2481 (4)	
C(44)	−1868 (7)	2934 (4)	2312 (5)	
C(45)	−2368 (8)	3213 (5)	2903 (5)	
C(46)	−1733 (11)	3395 (5)	3635 (5)	
C(47)	−584 (10)	3272 (5)	3797 (5)	
C(48)	−67 (8)	2994 (4)	3228 (4)	
C(49)	513 (6)	−66 (3)	2461 (4)	
C(50)	1553 (6)	−38 (4)	3131 (5)	
C(51)	2012 (9)	3258 (6)	1866 (9)	7.50
C(52)	878 (7)	3233 (5)	1481 (7)	6.50
H(11A)	−86 (6)	149 (4)	328 (4)	2.13
H(11B)	13 (6)	111 (4)	368 (4)	2.13
H(21A)	345 (6)	143 (4)	416 (4)	2.52
H(21B)	222 (6)	157 (4)	413 (4)	2.52
H(2B)	186 (6)	4 (4)	535 (4)	4.03
H(31A)	373 (6)	165 (4)	174 (5)	3.94
H(31B)	311 (6)	201 (4)	97 (5)	3.94
H(3B)	456 (7)	351 (5)	75 (5)	5.09
H(41A)	−61 (6)	201 (4)	55 (4)	3.44
H(41B)	−157 (6)	201 (4)	97 (4)	3.44
H(4B)	−103 (6)	390 (5)	−18 (4)	4.98
H(5A)	646 (7)	370 (5)	62 (5)	5.19
H(5B)	577 (7)	438 (5)	40 (5)	5.19
H(14)	−248 (6)	131 (4)	225 (4)	3.25
H(15)	−415 (6)	117 (4)	130 (4)	3.37
H(16)	−418 (7)	44 (4)	15 (5)	4.98
H(17)	−242 (7)	−4 (4)	−4 (5)	4.54
H(18)	−74 (6)	11 (4)	88 (4)	3.08
H(24)	476 (6)	75 (4)	388 (5)	4.09
H(25)	634 (7)	17 (4)	351 (5)	4.32
H(26)	624 (7)	−42 (4)	231 (5)	4.23
H(27)	444 (7)	−47 (5)	142 (5)	4.82
H(28)	281 (7)	8 (4)	173 (5)	3.90
H(34)	496 (6)	200 (4)	285 (5)	4.34
H(35)	629 (8)	216 (5)	400 (5)	6.98
H(36)	576 (8)	287 (5)	495 (6)	7.61
H(37)	393 (8)	351 (5)	476 (6)	7.58
H(38)	264 (7)	329 (5)	356 (5)	6.50
H(44)	−231 (6)	277 (4)	179 (5)	3.66
H(45)	−319 (7)	328 (5)	279 (5)	5.27
H(46)	−209 (7)	359 (5)	405 (5)	5.78
H(47)	−13 (7)	342 (5)	429 (5)	5.58
H(48)	77 (7)	292 (4)	335 (5)	4.11
H(49A)	78 (6)	−18 (4)	198 (4)	2.68
H(49B)	1 (6)	−43 (4)	257 (4)	2.68
H(50A)	199 (6)	−47 (4)	315 (4)	2.86
H(50B)	135 (6)	−6 (4)	363 (4)	2.86

(for $h0l$, $l = 2n + 1$; for $0k0$, $k = 2n + 1$) determined the space group $P2_1/c$ (No. 14) with $Z = 4$ and calculated density of 1.554 g cm^{-3} (d_{obsd} = 1.546 g cm^{-3}, measured by flotation in bromoform/benzene).

Intensity measurement was carried out for one quadrant of reciprocal space ($\pm h,k,l$) up to $2\theta = 42°$ with the same diffractometer by the ω–2θ scan technique. The individual scan speeds were determined by a short measurement at Kα_1 Bragg peak and varied from 1.6 to 29.3° min^{-1} in 2θ. The measurement interval was 1° below Kα_1 to 1° above Kα_2 of the Mo Kα doublet. The right and left backgrounds of the reflection were measured for half the time of the peak measurement. The intensities of three standard reflections, monitored after every 47 reflections, did not show any significant fluctuation during the collection procedure. A total of 4078 reflections were collected; 3065 of these for which $I > 1.96\sigma(I)$ were employed in the analysis ($\sigma(I)$ was calculated from the counting statistics), the remaining 1013 were considered "unobserved". The intensity data were corrected for Lorentz–polarization factor. No correction for absorption was applied (μ = 26.3 cm^{-1}).

The positions of the Br and Ni atoms were obtained from a three-dimensional Patterson synthesis. The remaining nonhydrogen atoms were located by a Fourier synthesis and refined by the full-matrix least-squares method with use of isotropic temperature factors. The electron density map now calculated showed well-defined regions for all atoms except the two methylene carbons C(51) and C(52) belonging to the same chelate ring, which were displayed as diffuse density regions, characteristic of disorder. In the further treatment, these two atoms were refined isotropically and all the others anisotropically. The refinement was continued until the changes of the parameters were ≤0.3 of their esd's. The next difference map yielded 37 hydrogen atom positions. The four hydrogen atoms belonging to the disordered methylene groups were not located. All the 37 hydrogen atoms were assigned the final isotropic thermal parameter of the adjacent carbon or oxygen atom. The final refinement of the atomic positions reached convergence at $R = 0.046$ and $R_w = 0.058$ where $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and $w = \sigma_{F_o}^{-2}$. A final difference map showed four highest peaks (0.35–0.55 e Å^{-3}) close to the disordered carbons C(51), C(52). Scattering factors of neutral atoms were taken from "International Tables for X-ray Crystallography". All calculations were performed on an ICL 4-72 computer with use of standard programs.[14]

A table of observed and calculated structure factors and a table of anisotropic thermal parameters is available as supplementary material.

Results and Discussion

The final atomic coordinates are presented in Table I. A summary of the intermolecular distances and angles is given in Table II, the labelling scheme being shown in Figure 1.

(14) The programs used include a local version of Fourier analysis (Sklenář, Prague, 1973), ORFLS and ORFFE (Busing, Martin and Levy), and a local version of ORTEP (Johnson).

Table II. Interatomic Distances (Å) and Angles (Deg) and Their Esd's

Coordination Polyhedron					
Ni-Br	2.587 (1)	P(1)-Ni-Br	92.28 (5)	P(1)-Ni-P(2)	83.91 (7)
Ni-P(1)	2.225 (2)	P(2)-Ni-Br	105.59 (5)	P(1)-Ni-P(3)	171.98 (7)
Ni-P(2)	2.236 (2)	P(3)-Ni-Br	95.74 (6)	P(1)-Ni-P(4)	92.48 (7)
Ni-P(3)	2.232 (2)	P(4)-Ni-Br	95.27 (6)	P(2)-Ni-P(3)	93.93 (7)
Ni-P(4)	2.215 (2)	P(2)-Ni-P(4)	158.94 (7)	P(3)-Ni-P(4)	86.77 (7)
Phosphorus Atoms					
P(1)-C(49)	1.817 (7)	Ni-P(1)-C(49)	103.7 (2)	C(49)-P(1)-C(11)	106.6 (3)
P(1)-C(11)	1.833 (7)	Ni-P(1)-C(11)	112.1 (2)	C(49)-P(1)-C(13)	104.9 (3)
P(1)-C(13)	1.824 (7)	Ni-P(1)-C(13)	123.3 (2)	C(11)-P(1)-C(13)	105.0 (3)
P(2)-C(50)	1.863 (7)	Ni-P(2)-C(50)	108.9 (2)	C(50)-P(2)-C(21)	105.1 (3)
P(2)-C(21)	1.843 (7)	Ni-P(2)-C(21)	112.9 (2)	C(50)-P(2)-C(23)	101.4 (3)
P(2)-C(23)	1.824 (7)	Ni-P(2)-C(23)	120.0 (2)	C(21)-P(2)-C(23)	107.0 (3)
P(3)-C(51)	1.821 (11)	Ni-P(3)-C(51)	108.8 (4)	C(51)-P(3)-C(31)	108.3 (5)
P(3)-C(31)	1.828 (9)	Ni-P(3)-C(31)	111.9 (3)	C(51)-P(3)-C(33)	102.4 (5)
P(3)-C(33)	1.820 (8)	Ni-P(3)-C(33)	120.6 (3)	C(31)-P(3)-C(33)	104.0 (4)
P(4)-C(52)	1.828 (10)	Ni-P(4)-C(52)	107.8 (3)	C(52)-P(4)-C(41)	101.3 (4)
P(4)-C(41)	1.828 (8)	Ni-P(4)-C(41)	117.2 (2)	C(52)-P(4)-C(43)	107.5 (4)
P(4)-C(43)	1.829 (7)	Ni-P(4)-C(43)	115.3 (2)	C(41)-P(4)-C(43)	106.5 (4)
Bridging Methylene Groups					
C(49)-C(50)	1.523 (11)	P(1)-C(49)-C(50)	107.6 (4)		
C(49)-H(49A)	0.98 (7)	C(49)-C(50)-P(2)	109.2 (4)		
C(49)-H(49B)	0.95 (7)	P(3)-C(51)-C(52)	114.7 (7)		
C(50)-H(50A)	0.95 (7)	C(51)-C(52)-P(4)	115.5 (7)		
C(50)-H(50B)	0.95 (7)				
C(51)-C(52)	1.397 (16)				
CH_2COO Groups					
C(11)-C(12)	1.539 (10)	P(1)-C(11)-C(12)	116.5 (4)		
C(11)-H(11A)	0.95 (8)	C(11)-C(12)-O(1A)	121.2 (5)		
C(11)-H(11B)	0.93 (7)	C(11)-C(12)-O(1B)	114.3 (5)		
C(12)-O(1A)	1.210 (8)	O(1A)-C(12)-O(1B)	124.5 (6)		
C(12)-O(1B)	1.277 (8)				
C(21)-C(22)	1.506 (10)	P(2)-C(21)-C(22)	112.7 (4)		
C(21)-H(21A)	0.98 (8)	C(21)-C(22)-O(2A)	124.3 (6)		
C(21)-H(21B)	0.94 (7)	C(21)-C(22)-O(2B)	111.5 (6)		
C(22)-O(2A)	1.198 (9)	O(2A)-C(22)-O(2B)	124.2 (6)		
C(22)-O(2B)	1.320 (9)				
C(31)-C(32)	1.511 (13)	P(3)-C(31)-C(32)	117.7 (6)		
C(31)-H(31A)	0.93 (8)	C(31)-C(32)-O(3A)	120.5 (7)		
C(31)-H(31B)	0.95 (8)	C(31)-C(32)-O(3B)	115.8 (7)		
C(32)-O(3A)	1.206 (10)	O(3A)-C(32)-O(3B)	123.7 (7)		
C(32)-O(3B)	1.296 (11)				
C(41)-C(42)	1.510 (10)	P(4)-C(41)-C(42)	115.9 (5)		
C(41)-H(41A)	0.94 (7)	C(41)-C(42)-O(4A)	121.7 (6)		
C(41)-H(41B)	0.98 (7)	C(41)-C(42)-O(4B)	115.3 (6)		
C(42)-O(4A)	1.189 (10)	O(4A)-C(42)-O(4B)	123.0 (7)		
C(42)-O(4B)	1.265 (9)				
Phenyl Groups					
C(13)-C(14)	1.379 (10)	C(13)-C(14)-C(15)	121.1 (6)		
C(14)-C(15)	1.376 (11)	C(14)-C(15)-C(16)	119.8 (7)		
C(15)-C(16)	1.378 (12)	C(15)-C(16)-C(17)	119.3 (7)		
C(16)-C(17)	1.368 (12)	C(16)-C(17)-C(18)	121.6 (7)		
C(17)-C(18)	1.386 (11)	C(17)-C(18)-C(13)	118.8 (6)		
C(18)-C(13)	1.388 (10)	C(18)-C(13)-C(14)	119.3 (6)		
C(23)-C(24)	1.392 (10)	C(23)-C(24)-C(25)	119.2 (7)		
C(24)-C(25)	1.396 (12)	C(24)-C(25)-C(26)	121.7 (7)		
C(25)-C(26)	1.363 (12)	C(25)-C(26)-C(27)	119.8 (7)		
C(26)-C(27)	1.392 (12)	C(26)-C(27)-C(28)	119.8 (7)		
C(27)-C(28)	1.387 (12)	C(27)-C(28)-C(23)	120.4 (6)		
C(28)-C(23)	1.384 (10)	C(28)-C(23)-C(24)	119.7 (6)		
C(33)-C(34)	1.385 (12)	C(33)-C(34)-C(35)	122.8 (8)		
C(34)-C(35)	1.381 (14)	C(34)-C(35)-C(36)	117.9 (1.1)		
C(35)-C(36)	1.314 (19)	C(35)-C(36)-C(37)	125.4 (1.2)		
C(36)-C(37)	1.350 (23)	C(36)-C(37)-C(38)	116.1 (1.1)		
C(37)-C(38)	1.427 (18)	C(37)-C(38)-C(33)	121.4 (1.0)		
C(38)-C(33)	1.387 (13)	C(38)-C(33)-C(34)	116.3 (8)		
C(43)-C(44)	1.391 (11)	C(43)-C(44)-C(45)	118.5 (7)		
C(44)-C(45)	1.395 (13)	C(44)-C(45)-C(46)	121.2 (8)		
C(45)-C(46)	1.377 (13)	C(45)-C(46)-C(47)	119.3 (9)		
C(46)-C(47)	1.383 (18)	C(46)-C(47)-C(48)	120.8 (8)		
C(47)-C(48)	1.376 (13)	C(47)-C(48)-C(43)	119.8 (8)		
C(48)-C(43)	1.392 (10)	C(48)-C(43)-C(44)	120.3 (7)		

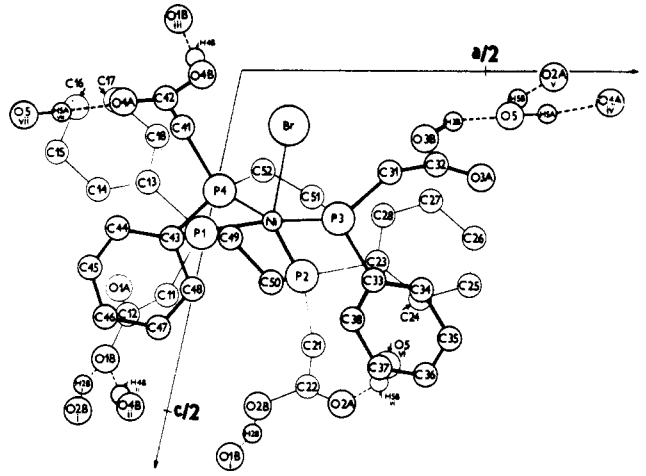

Figure 1. The projection of the structure onto the *ac* plane. The dashed lines indicate intermolecular hydrogen bonding. Symmetry code: (i) $-x, -y, 1-z$; (ii) $x, {}^1/_2-y, {}^1/_2+z$; (iii) $x, {}^1/_2-y, z-{}^1/_2$; (iv) $1+x, y, z$; (v) $1-x, {}^1/_2+y, {}^1/_2-z$; (vi) $1-x, y-{}^1/_2, {}^1/_2-z$; (vii) $x-1, y, z$; (viii) $-x, {}^1/_2+y, {}^1/_2-z$.

Table III. Least-Squares Planes and Deviations (Å) of Atoms Therefrom[a]

atom	dev	atom	dev
Plane I: $0.2818X - 0.4240Y - 0.8670Z = -4.5373$			
P(1)[b]	0.127	P(3)[b]	0.122
P(2)[b]	−0.125	P(4)[b]	−0.124
Ni	0.280	Br	2.854
C(11)	−1.612	C(31)	1.684
C(13)	0.918	C(33)	−1.149
C(21)	−1.880	C(41)	1.097
C(23)	0.915	C(43)	−1.766
C(49)	0.899	C(51)	−0.270
C(50)	0.101	C(52)	−0.008
Plane II: $0.2925X + 0.8306Y - 0.4738Z = -0.9150$			
C(13)[b]	−0.003	C(16)[b]	−0.010
C(14)[b]	−0.004	C(17)[b]	0.003
C(15)[b]	0.010	C(18)[b]	0.003
P(1)	−0.027		
Plane III: $0.3088X + 0.8521Y - 0.4227Z = -0.2638$			
C(23)[b]	0.000	C(26)[b]	0.003
C(24)[b]	0.000	C(27)[b]	−0.003
C(25)[b]	−0.002	C(28)[b]	0.001
P(2)	−0.111		
Plane IV: $0.4684X + 0.7839Y - 0.4076Z = 3.1452$			
C(33)[b]	−0.014	C(36)[b]	−0.014
C(34)[b]	0.012	C(37)[b]	0.011
C(35)[b]	0.002	C(38)[b]	0.003
P(3)	0.131		
Plane V: $0.2049X + 0.9277Y - 0.3121Z = 3.1151$			
C(43)[b]	0.009	C(46)[b]	0.014
C(44)[b]	−0.001	C(47)[b]	−0.006
C(45)[b]	−0.010	C(48)[b]	−0.005
P(4)	0.034		

[a] Cartesian (Å) coordinates (X, Y, Z) are related to the fractional cell coordinates (x, y, z) by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & 0 & c\cos\beta \\ 0 & b & 0 \\ 0 & 0 & c\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

[b] Atoms included in calculating the plane.

Table III summarizes and characterizes important planar moieties in the structure.

The Coordination Polyhedron. As can be seen from Figure 2, the distorted tetragonal pyramid of the donor atoms consists of four approximately coplanar phosphorus atoms and bromide at the top. Owing to the steric requirements of the diphosphine ligand, the basal plane is distorted, with individual phosphorus atoms being displaced by ±0.12 Å from the ideal plane. The nickel atom is located at 0.28 Å and bromine atom at 2.85 Å above the approximate center of the basal square. This arrangement is very similar to that of $[NiI(Et_2PCH_2CH_2PEt_2)_2]I$.[15] No intra- or intermolecular contacts can be assumed to occupy the sixth coordination site as the nearest such interaction exceeds 5 Å.

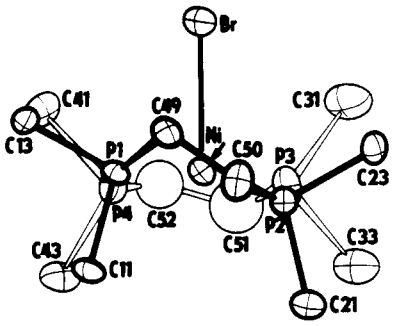

Figure 2. $NiBr(C_2PCCPC_2)_2$ core of the complex showing the disordered methylene carbons and the configuration of the complex (ORTEP diagram; 50% ellipsoids). P–Ni bonds are not shown for clarity.

Table IV. Torsion Angles (Deg) within Chelate Rings

	NiP(1)C(49)-C(50)P(2)	NiP(3)C(51)-C(52)P(4)
τ(Ni–P)	−37	1
τ(P–C)	56	−18[a]
τ(C–C)	−44	29[a]
τ(C–P)	14	−26[a]
τ(P–Ni)	16	11

[a] The angles around atoms affected by disorder.

The Ligands. Stereochemically, both phosphine ligands correspond to the meso-diastereoisomer with respect to the chiral phosphorus atoms, and the whole complex adopts the anti-bis(meso-ligand) configuration.[16,17] This corresponds formally to the (*RS*:*SR*)-isomer if labeled from P(1) to P(4). It is interesting to note that a similar chiral bis(tertiary phosphine), *meso*-bis(methylphenyl)diphosphinoethane (L) also forms an analogous pentacoordinate nickel(II) complex, $[Ni(SCN)L_2](SCN)$, the limited solubility of which was employed in the separation of the diastereoisomers of the ligand.[18] In at least two ways, the phosphine ligands in the same molecule are not equivalent. First, the electroneutrality of the complex requires that one ligand be the mononegative anion HQ^- and the second the acid H_2Q; this rather formal difference is strongly counterbalanced by intermolecular hydrogen bonding (vide infra). Second, a structurally more important difference consists in the conformation and thermal vibration parameters of the chelate rings and of further atoms bonded to the phosphorus atom involved. The difference is obvious from Figure 2 and Table IV where corresponding torsion angles are summarized. While the ring involving P(1)C(49)C(50)P(2) appears quite normal with λ-skew conformation, the second ring P(3)C(51)C(52)P(4) is strongly affected by disorder of the bridging carbon atoms, especially of C(51). The disorder further affects the phenyl ring C(33)-C(38) where anomalously high temperature factors and errors in the atomic coordinates were also observed, most markedly with

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(16) Bercz, J. P.; Horner, L.; Bercz, C. V. *Justus Liebigs Ann. Chem.* **1967**, *703*, 17.
(17) Groth, P. *Acta Chem. Scand.* **1970**, *24*, 2785.
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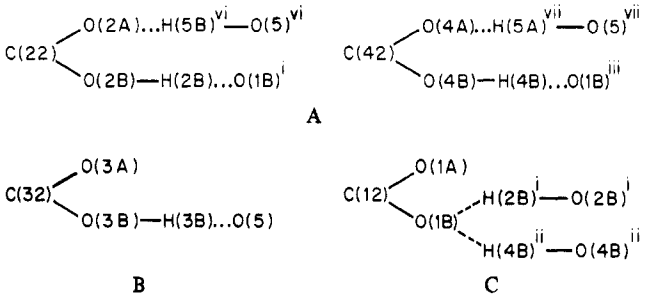
Table V. Distances (Å) and Angles (Deg) of Hydrogen Bonds and Their Esd's[a]

bond	O–H	H···O	O···O	angle OHO
O(2B)–H(2B)···O(1B)^{i}	1.21 (7)	1.41 (7)	2.591 (7)	162 (4)
O(5)^{vi}–H(5B)^{vi}···O(2A)	0.99 (9)	1.88 (9)	2.824 (9)	159 (6)
O(4B)–H(4B)···O(1B)^{iii}	1.21 (8)	1.41 (8)	2.506 (8)	146 (5)
O(5)^{vii}–H(5A)^{vii}···O(4A)	0.98 (9)	1.77 (9)	2.749 (10)	171 (6)
O(3B)–H(3B)···O(5)	0.97 (9)	1.62 (9)	2.541 (10)	158 (6)

[a] For symmetry code, see Figure 1.

the *p*-carbon C(36). A similar disorder of bridging methylene groups in complexes of chelating disphosphines has been described,[19] but the reasons for it remained obscure. It should be pointed out here that there are relatively short intermolecular contacts of C(51) and C(52) with O(1A)^{viii} ranging from 3.01 to 3.13 Å. It seems reasonable that these intermolecular contacts on the one hand and the tendency of the chelate rings to adopt the statistically preferred λ,δ-conformation[20] on the other hand are the counterbalancing factors that are responsible for the disorder, even in the solid state. Logically, the thermal motion of the bridging atoms further influences the neighboring phenyl group, rather than the $-CH_2CO_2H$ group which is more rigid because of hydrogen bonding.

Hydrogen Bonding. The main difference between the complex studied and analogous complexes of simple bis(tertiary phosphines) consists in the presence of the carboxyl groups and water molecule that are not coordinated to nickel but involved in a system of hydrogen bonding (see Figure 1) which holds the whole structure together. The water molecule is bonded intramolecularly through O(5) to H(3B) and by two further unequal intermolecular bonds to O(2A)^{v} and O(4A)^{iv}. According to the empirical relation,[21] the lengths of these two hydrogen bonds correspond fairly well to the two $\nu(H_2O)$ bands in the IR spectrum. The system of intermolecular carboxyl-to-carboxyl interactions includes three different moieties A, B, and C. As can be seen from Table V, where relevant



distances and angles are summarized, the hydrogen bonds are more symmetrical than those in, e.g., alkali-metal hydrogen carboxylates. Hence, their lengths alone are of little value for distinguishing between intramolecular and intermolecular O–H bonding (i.e., protonized and dissociated carboxyl, respectively). Because of the stereochemical difference between phosphorus atoms it becomes necessary, at least for nomenclatural reasons, to define one of the carboxyl groups as dissociated. The detailed inspection of hydrogen bonding and of the orientation of the carboxyl groups relative to the plane of the phosphorus atoms suggests the C type (trans to the water molecule) as the dissociated carboxyl. This moiety involves three oxygens sharing two hydrogen atoms that yield a net negative charge compensating the excessive positive charge on nickel. From this point of view, the whole complex can be looked at as a zwitterion.

Registry No. $[NiBr(HQ)(H_2Q)]\cdot H_2O$, 77080-88-7.

Supplementary Material Available: listings of structure factor amplitudes and anisotropic thermal parameters (25 pages). Ordering information is given on any current masthead page.

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