

Tableau 3. Comparaison de quelques polyèdres, NNNMXY, avec les trois modèles idéalisés

Angles (°)	Composé									p.b.c.	p.i.d.	b.p.t.
	(1)*	(2)	(3)*	(4)	(5)	(6)	(7)*	(8)	(9)			
Cl(1)MN(2)	115,5	121,5	125	143	150	157	160	162	178	180	160	120
N(1)MN(3)	132,9	149,1	152	145	147	146	157	157	162	180	160	180
Cl(2)MN(1)	97,6	98,2	98	102	102	99	96	96	91,5	90	100	90
Cl(2)MN(3)	99,2	97,8	98	93	96	100	93	95	97,6	90	100	90
Cl(2)MN(2)	112,1	121,5	125	105	99	94	101	97	93,8	90	100	120
Cl(2)MCl(1)	132	117,1	111	112	111	110	99	101	90,1	90	100	120
N(1)MN(2)	66,2	75,5	76	74	74	74	78	80	79,1	90	90	90
N(2)MN(3)	66,7	74,5	76	73	76	75	80	80	82,3	90	88	90
N(1)MCl(1)	100,3	98,2	98	97	97	100	98	98	100,0	90	88	90
N(3)MCl(1)	99,9	97,8	98	101	102	102	100	99	97,3	90	88	90
$\sum \Delta\alpha$ (p.b.c.)	128,4	117,1	111	74	60	47	40	36	5,9			
$\sum \Delta\alpha$ (p.i.d.)	88,6	80,1	71	34	22	19	2	6	34,1			
$\sum \Delta\alpha$ (b.p.t.)	14,6	5,9	19	46	60	73	80	84	114,1			
% p.i.d.	26	33	41	72	82	84	99,8	99,5	72			

Composés: (1) Cd(tpy)[Mn(CO)<sub>5</sub>]; (2) Zn(tpy)Cl<sub>2</sub> (I); (3) Co(tpy)(CNO)<sub>2</sub>; (4) Zn(tpy)Cl<sub>2</sub> (II); (5) Co(tpy)Cl<sub>2</sub>; (6) Co(paphy)Cl<sub>2</sub>; (7) [Cu(tpy)CN]NO<sub>3</sub>·H<sub>2</sub>O; (8) Cu(tpy)Cl<sub>2</sub>·H<sub>2</sub>O; (9) [Cu(tpy)Cl]PF<sub>6</sub>.

\* Cl est remplacé par CNO, CN, NO<sub>3</sub>.

p.b.c. C'est donc la forme I qui se rapproche le plus d'une bipyramide trigonale. La forme II peut être comparée à une pyramide idéale déformée. Dans les deux cas l'atome de zinc se trouve dans un plan formé par les atomes Cl, Cl', N(1) (forme I) ou C(11), C(12), N(2) (forme II). Ces grandes similitudes expliquent que l'on obtienne soit l'une soit l'autre des deux variétés selon les conditions de recristallisation.

En conclusion, il semble que les facteurs principaux qui déterminent la stéréochimie d'un cation soient: la répulsion électrostatique entre les ligandes, la nature des liaisons métal-ligande, la forme de la molécule, l'encombrement stérique et l'énergie de stabilisation du champ cristallin.

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## [Bis(2-diphenylphosphinoethyl)phenylphosphine]iodonickel(II) Tetraphenylborate, C<sub>34</sub>H<sub>33</sub>INiP<sub>3</sub><sup>+</sup>·C<sub>24</sub>H<sub>20</sub>B<sup>-</sup>, and [Bis(2-diphenylphosphinoethyl)phenylphosphine]chloronickel(II) Tetraphenylborate, C<sub>34</sub>H<sub>33</sub>ClNiP<sub>3</sub><sup>+</sup>·C<sub>24</sub>H<sub>20</sub>B<sup>-\*</sup>

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**Abstract.** [Ni(C<sub>34</sub>H<sub>33</sub>P<sub>3</sub>)I][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]: *M<sub>r</sub>* = 1039·41, triclinic, *P*1, *a* = 11·670 (1), *b* = 14·821 (2), *c* =

\* Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands. XIV.

17·191 (3) Å, α = 70·859 (7), β = 75·290 (8), γ = 65·21 (1)°, *V* = 2527 Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1·35, *D<sub>x</sub>* = 1·366 Mg m<sup>-3</sup>, *F*(000) = 1064, Mo *K*α, λ = 0·70926 Å, μ = 1·14 mm<sup>-1</sup>, *T* = 295 K, *R* = 0·039, 2131 unique

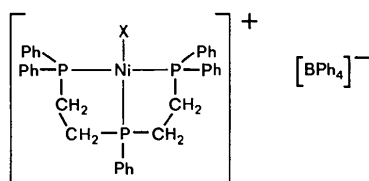
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reflexions.  $[Ni(C_{34}H_{33}P_3)Cl][B(C_6H_5)_4]$ :  $M_r = 947.96$ , triclinic,  $P\bar{1}$ ,  $a = 11.5899$  (6),  $b = 14.673$  (2),  $c = 17.139$  (1) Å,  $\alpha = 69.849$  (6),  $\beta = 74.772$  (4),  $\gamma = 65.384$  (5)°,  $V = 2463$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.25$ ,  $D_x = 1.278$  Mgm<sup>-3</sup>,  $F(000) = 992$ , Mo  $K\alpha$ ,  $\lambda = 0.70926$  Å,  $\mu = 0.58$  mm<sup>-1</sup>,  $T = 295$  K,  $R = 0.062$ , 2964 unique reflexions. For the related compound.  $[Ni(C_{34}H_{33}P_3)Br][B(C_6H_5)_4]$ ,  $M_r = 992.41$ ,  $a = 11.6251$  (7),  $b = 14.715$  (2),  $c = 17.159$  (2) Å,  $\alpha = 70.209$  (7),  $\beta = 74.881$  (5),  $\gamma = 65.076$  (7)°,  $V = 2481$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.32$ ,  $D_x = 1.329$  Mgm<sup>-3</sup>,  $F(000) = 1028$ , Mo  $K\alpha$ ,  $\lambda = 0.70926$  Å,  $T = 295$  K. For  $[Ni(C_{34}H_{33}P_3)I][B(C_6H_5)_4]$  only the cell parameters were determined. In the isotopic compounds  $[Ni(C_{34}H_{33}P_3)I][B(C_6H_5)_4]$  and  $[Ni(C_{34}H_{33}P_3)Cl][B(C_6H_5)_4]$  one halogen atom and three P atoms from one ligand molecule  $\{[(C_6H_5)_2P(CH_2)_2]_2P(C_6H_5)\}$ , denoted (ppp) are coordinated to Ni in a square-planar manner. In the monomeric complex ions  $[Ni(ppp)X]^+$ ,  $X = Cl$  and  $I$ , Ni takes part in two fused five-membered chelate rings (NiPC<sub>2</sub>P). All interatomic distances and angles are normal. The compounds are diamagnetic.

**Introduction.** Nickel(II) halides and tridentate linear ligands often form four- and five-coordinated complexes of the type  $[NiLX]^+$  and  $NiLX_2$ , where  $X$  is a halogen atom (Morassi, Bertini & Sacconi, 1973). The four-coordinated  $[NiLX]^+$  complexes are, with low-electronegative donor atoms, mostly square planar (Orioli, 1971). In the compound [bis(2-diphenylphosphinoethyl)phenylphosphine](*O*-methylsulphinato)-nickel(II) tetraphenylborate,  $[Ni(ppp)OS(O)CH_3][B(C_6H_5)_4]$ , the square-planar cation shows distortions, probably caused by geometric requirements of the ligand and steric repulsion between the terminal phenyl groups and the methylsulphinate group (Mealli, Peruzzini & Stoppioni, 1980).

The structure determinations of the title compounds



were performed in order to study the coordination polyhedron of Ni and the distortions from it. This investigation is part of a study of complexes between transition-metal halides and substituted phosphines or related ligands.

**Experimental.** Values are given for  $[Ni(ppp)I][B(C_6H_5)_4]$  and (in parentheses if they differ) for  $[Ni(ppp)Cl][B(C_6H_5)_4]$ : Brown (orange) crystals in the form of plates (from  $C_2H_5OH/CH_2Cl_2$ ),  $D_m$  by

flotation,  $0.15 \times 0.27 \times 0.07$  mm ( $0.22 \times 0.37 \times 0.09$  mm), Enraf-Nonius CAD-4 diffractometer, Mo  $K\alpha$  graphite monochromator  $\lambda = 0.70926$  Å, cell parameters from 50 accurately measured  $\theta$  values, Lp and absorption corrections, transmission factors 0.82–0.94 (0.88–0.95); 6431 (6179) unique reflexions in the  $\theta$  interval 3–22°, 2131 (2964) with  $I \geq 3\sigma(I)$ ; the three standard reflexions showed a 4% decrease; direct methods (MULTAN, Germain, Main & Woolfson, 1971), successive electron-density maps for B and C atoms, H atoms geometrically generated (SHELX, Sheldrick, 1976), least-squares refinement with SHELX,  $w^{-1} = \sigma^2(F)$ , scattering factors for non-H from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965); 176 parameters,  $R = 0.039$  (0.062),  $R_w = 0.047$  (0.073), highest residuals 0.3 (0.4) eÅ<sup>-3</sup> and deepest pits 0.3 (0.4) eÅ<sup>-3</sup>, correction for anomalous dispersion (Cromer & Liberman, 1970); the intensities show no indication of extinction; magnetic susceptibilities were obtained with a Faraday balance (Blom & Hörlin, 1977),  $\chi_{mass} = -0.3$  (8)  $\times 10^{-8}$  [ $-0.9$  (5)  $\times 10^{-8}$ ] m<sup>3</sup>kg<sup>-1</sup>.

**Discussion.** Final positional parameters for  $[Ni(C_{34}H_{33}P_3)I][B(C_6H_5)_4]$  are given in Table 1.\* Selected interatomic distances and angles are given in Fig. 1 (a) and (b) and Table 2. A view of the atomic arrangement in  $[Ni(ppp)I]^+$  and a stereoview of the packing of  $[Ni(ppp)I][B(C_6H_5)_4]$  in the unit cell are given in Figs. 2 and 3 (Johnson, 1965). In the title compounds the Ni atoms are four coordinated in a square-planar manner. When (ppp) acts as a tridentate ligand in the monomeric complexes two fused five-membered chelate rings are formed. The halide ions constitute the fourth corner in the square plane (Figs. 1 and 2). From the positional parameters it is clear that the I and Cl compounds are isotopic. The Br compound is presumably also isotopic in view of the cell parameters. The Ni atoms are situated 0.052 (2) and 0.064 (1) Å outside the least-squares planes formed by the donor atoms of the ions  $[Ni(ppp)I]^+$  and  $[Ni(ppp)Cl]^+$ , respectively, Table 3. The phenyl rings as well as the C atoms of the five-membered chelate rings are not symmetric with respect to a plane of symmetry through  $X$ , Ni, P(2) and C(17). There are no significant differences in analogous Ni–P distances in the two compounds, but there is a highly significant difference between the Ni–central P and the Ni–terminal P distances, 2.121 (2) Å, mean, and 2.209 (2) Å, mean, respectively. The corresponding distances in

\* Lists of structure factors, anisotropic thermal parameters, fractional coordinates and isotropic temperature factors for the H atoms and final positional parameters for  $[Ni(C_{34}H_{33}P_3)Cl][B(C_6H_5)_4]$  have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38322 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and isotropic temperature factors for the non-hydrogen atoms in  $[\text{Ni}(\text{C}_{34}\text{H}_{33}\text{P}_3)\text{I}][\text{B}(\text{C}_6\text{H}_5)_4]$

The values for H have been deposited. E.s.d.'s are in parentheses. For I, Ni, P(1), P(2) and P(3) the isotropic mean values of  $U_{ij}$  are given, calculated according to Willis & Pryor (1975).

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{Å}^2)$
I	0.5960 (1)	0.73289 (8)	0.43069 (6)	0.0646 (6)
Ni	0.7663 (1)	0.7342 (1)	0.31019 (9)	0.399 (9)
P(1)	0.7818 (3)	0.8733 (3)	0.3200 (2)	0.043 (2)
P(2)	0.9372 (3)	0.7180 (2)	0.2261 (2)	0.039 (2)
P(3)	0.7507 (3)	0.6182 (3)	0.2627 (2)	0.045 (2)
C(1)	0.936 (1)	0.8804 (9)	0.2640 (7)	0.046 (3)
C(2)	0.965 (1)	0.8384 (8)	0.1867 (7)	0.048 (4)
C(3)	0.939 (1)	0.6642 (8)	0.1449 (7)	0.042 (3)
C(4)	0.895 (1)	0.5749 (9)	0.1893 (7)	0.050 (4)
C(5)	0.6647 (7)	0.9853 (7)	0.2637 (5)	0.040 (3)
C(6)	0.5596 (7)	0.9780 (7)	0.2454 (5)	0.059 (4)
C(7)	0.4700 (7)	1.0649 (7)	0.2019 (5)	0.075 (4)
C(8)	0.4857 (7)	1.1591 (7)	0.1767 (5)	0.073 (4)
C(9)	0.5908 (7)	1.1663 (7)	0.1950 (5)	0.083 (5)
C(10)	0.6804 (7)	1.0794 (7)	0.2385 (5)	0.070 (4)
C(11)	0.7682 (7)	0.8886 (5)	0.4210 (5)	0.043 (3)
C(12)	0.6738 (7)	0.9725 (5)	0.4481 (5)	0.059 (4)
C(13)	0.6626 (7)	0.9786 (5)	0.5291 (5)	0.075 (4)
C(14)	0.7458 (7)	0.9009 (5)	0.5830 (5)	0.086 (5)
C(15)	0.8402 (7)	0.8171 (5)	0.5559 (5)	0.083 (5)
C(16)	0.8514 (7)	0.8110 (5)	0.4748 (5)	0.070 (4)
C(17)	1.0716 (7)	0.6284 (7)	0.2791 (5)	0.044 (3)
C(18)	1.1953 (7)	0.6139 (7)	0.2383 (5)	0.071 (4)
C(19)	1.2992 (7)	0.5404 (7)	0.2779 (5)	0.097 (5)
C(20)	1.2794 (7)	0.4814 (7)	0.3584 (5)	0.112 (6)
C(21)	1.1557 (7)	0.4959 (7)	0.3993 (5)	0.120 (6)
C(22)	1.0518 (7)	0.5694 (7)	0.3596 (5)	0.081 (5)
C(23)	0.619 (1)	0.6793 (7)	0.2000 (5)	0.052 (4)
C(24)	0.637 (1)	0.6626 (7)	0.1217 (5)	0.080 (5)
C(25)	0.537 (1)	0.7090 (7)	0.0745 (5)	0.111 (6)
C(26)	0.418 (1)	0.7721 (7)	0.1056 (5)	0.088 (5)
C(27)	0.400 (1)	0.7888 (7)	0.1839 (5)	0.113 (6)
C(28)	0.500 (1)	0.7424 (7)	0.2311 (5)	0.107 (6)
C(29A)	0.736 (2)	0.501 (2)	0.342 (1)	0.06 (2)
C(30A)	0.809 (2)	0.452 (2)	0.407 (1)	0.13 (1)
C(31A)	0.799 (2)	0.363 (2)	0.464 (1)	0.14 (1)
C(32A)	0.716 (2)	0.322 (2)	0.456 (1)	0.10 (3)
C(33A)	0.642 (2)	0.371 (2)	0.391 (1)	0.10 (1)
C(34A)	0.652 (2)	0.460 (2)	0.334 (1)	0.082 (9)
C(29B)	0.729 (1)	0.508 (1)	0.331 (1)	0.04 (2)
C(30B)	0.836 (1)	0.420 (1)	0.353 (1)	0.039 (7)
C(31B)	0.822 (1)	0.335 (1)	0.414 (1)	0.052 (7)
C(32B)	0.700 (1)	0.337 (1)	0.452 (1)	0.08 (2)
C(33B)	0.593 (1)	0.424 (1)	0.430 (1)	0.069 (9)
C(34B)	0.608 (1)	0.510 (1)	0.369 (1)	0.040 (7)
C(35)	0.1204 (7)	0.1348 (5)	0.0724 (5)	0.041 (3)
C(36)	0.0797 (7)	0.0627 (5)	0.0643 (5)	0.049 (4)
C(37)	0.1546 (7)	-0.0025 (5)	0.0126 (5)	0.055 (4)
C(38)	0.2702 (7)	0.0046 (5)	-0.0310 (5)	0.061 (4)
C(39)	0.3109 (7)	0.0768 (5)	-0.0229 (5)	0.057 (4)
C(40)	0.2360 (7)	0.1419 (5)	0.0288 (5)	0.045 (3)
C(41)	0.0286 (6)	0.1220 (5)	0.2346 (5)	0.041 (3)
C(42)	0.1394 (6)	0.0356 (5)	0.2502 (5)	0.052 (4)
C(43)	0.1461 (6)	-0.0342 (5)	0.3281 (5)	0.069 (4)
C(44)	0.0419 (6)	-0.0176 (5)	0.3904 (5)	0.064 (4)
C(45)	-0.0689 (6)	0.0687 (5)	0.3748 (5)	0.062 (4)
C(46)	-0.0756 (6)	0.1385 (5)	0.2969 (5)	0.052 (4)
C(47)	-0.1186 (7)	0.2790 (5)	0.1133 (5)	0.045 (3)
C(48)	-0.2001 (7)	0.3486 (5)	0.1599 (5)	0.058 (4)
C(49)	-0.3225 (7)	0.4112 (5)	0.1400 (5)	0.073 (4)
C(50)	-0.3633 (7)	0.4042 (5)	0.0734 (5)	0.073 (4)
C(51)	-0.2818 (7)	0.3346 (5)	0.0267 (5)	0.070 (4)
C(52)	-0.1594 (7)	0.2719 (5)	0.0467 (5)	0.053 (4)
C(53)	0.0903 (7)	0.2913 (6)	0.1407 (4)	0.041 (3)
C(54)	0.1371 (7)	0.2832 (6)	0.2107 (4)	0.044 (3)
C(55)	0.1960 (7)	0.3493 (6)	0.2075 (4)	0.053 (4)
C(56)	0.2081 (7)	0.4235 (6)	0.1343 (4)	0.058 (4)
C(57)	0.1613 (7)	0.4316 (6)	0.0643 (4)	0.053 (4)
C(58)	0.1024 (7)	0.3655 (6)	0.0675 (4)	0.044 (3)
B	0.028 (1)	0.208 (1)	0.1397 (8)	0.036 (4)

Table 2. Angles ( $^\circ$ ) in the coordination polyhedra of Ni, P(1), P(2) and P(3)

E.s.d.'s are given in parentheses. For labelling, see Fig. 1 and Table 2.  $X = \text{I, Cl}$

	$[\text{Ni}(\text{ppp})\text{I}][\text{BPh}_4]$	$[\text{Ni}(\text{ppp})\text{Cl}][\text{BPh}_4]$
$X-\text{Ni}-\text{P}(1)$	93.8 (1)	93.7 (1)
$\text{P}(1)-\text{Ni}-\text{P}(2)$	85.6 (1)	85.6 (1)
$\text{P}(2)-\text{Ni}-\text{P}(3)$	85.8 (1)	85.6 (1)
$\text{P}(3)-\text{Ni}-X$	97.4 (1)	97.2 (1)
$X-\text{Ni}-\text{P}(2)$	168.2 (1)	171.6 (1)
$\text{P}(1)-\text{Ni}-\text{P}(3)$	163.7 (1)	162.4 (1)
$\text{Ni}-\text{P}(1)-\text{C}(1)$	109.2 (4)	108.7 (3)
$\text{Ni}-\text{P}(1)-\text{C}(5)$	108.8 (3)	108.7 (3)
$\text{Ni}-\text{P}(1)-\text{C}(11)$	118.4 (3)	117.1 (2)
$\text{C}(1)-\text{P}(1)-\text{C}(5)$	104.4 (5)	105.5 (4)
$\text{C}(1)-\text{P}(1)-\text{C}(11)$	106.7 (4)	108.2 (4)
$\text{C}(5)-\text{P}(1)-\text{C}(11)$	108.4 (4)	108.1 (3)
$\text{Ni}-\text{P}(2)-\text{C}(2)$	111.3 (4)	110.7 (3)
$\text{Ni}-\text{P}(2)-\text{C}(3)$	110.8 (4)	110.6 (3)
$\text{Ni}-\text{P}(2)-\text{C}(17)$	110.0 (3)	110.3 (3)
$\text{C}(2)-\text{P}(2)-\text{C}(3)$	113.5 (5)	112.8 (4)
$\text{C}(2)-\text{P}(2)-\text{C}(17)$	105.0 (5)	106.4 (4)
$\text{C}(3)-\text{P}(2)-\text{C}(17)$	106.0 (5)	105.9 (4)
$\text{Ni}-\text{P}(3)-\text{C}(4)$	108.0 (4)	109.1 (3)
$\text{Ni}-\text{P}(3)-\text{C}(23)$	109.8 (3)	108.6 (3)
$\text{Ni}-\text{P}(3)-\text{C}(29A)$	116.5 (6)	115.6 (5)
$\text{Ni}-\text{P}(3)-\text{C}(29B)$	120.9 (6)	121.0 (5)
$\text{C}(4)-\text{P}(3)-\text{C}(23)$	104.9 (5)	105.9 (4)
$\text{C}(4)-\text{P}(3)-\text{C}(29A)$	106.9 (7)	108.0 (6)
$\text{C}(4)-\text{P}(3)-\text{C}(29B)$	106.7 (6)	105.6 (5)
$\text{C}(23)-\text{P}(3)-\text{C}(29A)$	110.1 (7)	109.2 (5)
$\text{C}(23)-\text{P}(3)-\text{C}(29B)$	105.5 (6)	105.7 (5)

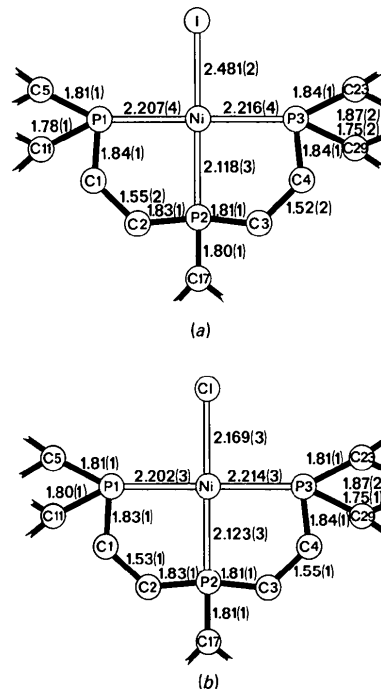


Fig. 1. Schematic drawings of the complex ions (a)  $[\text{Ni}(\text{ppp})\text{I}]^+$  and (b)  $[\text{Ni}(\text{ppp})\text{Cl}]^+$  showing interatomic distances (Å). The C-C distances in the phenyl rings (omitted in the drawings) are assumed to be 1.395 Å. The bonds of the ligand chain are drawn with heavy lines, those in the coordination polyhedra of Ni with double lines.

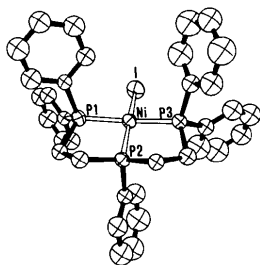


Fig. 2. A drawing of the complex ion  $[Ni(ppp)I]^+$ . The bonds of the ligand molecule, (ppp), are drawn with heavy lines, those in the coordination polyhedron of Ni with double lines. The phenyl ring C(29B)–C(34B) and the H atoms are omitted. The ellipsoids of I, Ni and P and the spheres of C are drawn to enclose 50% probability.

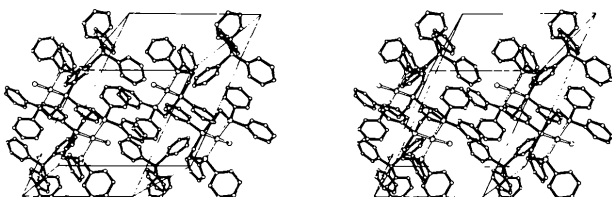


Fig. 3. A stereoview of the packing of  $[Ni(ppp)I][B(C_6H_5)_4]$  in the unit cell. The H atoms are omitted. (*x* is horizontal, from left to right; *z* is into the page).

Table 3. *The planarities of the coordination figures of Ni*

The halide ion,  $I^-$  or  $Cl^-$ , and the P atoms were used for the calculation of the least-squares planes. Deviations are in Å and e.s.d.'s are in parentheses.

$[Ni(ppp)I][BPh_4]$	$[Ni(ppp)Cl][BPh_4]$
Ni	Ni
I	Cl
P(1)	P(1)
P(2)	P(2)
P(3)	P(3)

Table 4. *Distances (Å) and angles (°) in the  $B(C_6H_5)_4^-$  ion*

E.s.d.'s are given in parentheses.

	$[Ni(ppp)I][BPh_4]$	$[Ni(ppp)Cl][BPh_4]$
B–C(35)	1.70 (2)	1.68 (1)
B–C(41)	1.71 (2)	1.69 (1)
B–C(47)	1.67 (2)	1.68 (1)
B–C(53)	1.69 (2)	1.70 (1)
C(35)–B–C(41)	104.9 (8)	105.5 (7)
C(35)–B–C(47)	112.3 (8)	111.9 (7)
C(35)–B–C(53)	110.8 (8)	111.2 (7)
C(41)–B–C(47)	113.6 (8)	113.1 (7)
C(41)–B–C(53)	109.4 (8)	109.7 (6)
C(47)–B–C(53)	105.9 (8)	105.6 (7)

$[Ni(ppp)OS(O)CH_3]^+$  are 2.111 (2) Å (Ni–central P) and 2.165 (2) Å, mean (Ni–terminal P). These distances are shorter, but the former by less than  $4\sigma$ . The terminal P atoms form two aromatic and one aliphatic and the central P one aromatic and two aliphatic P–C bonds. This and the different *trans* influencing effects of opposite atoms may be the origin of the differences in the Ni–P distances.

The Ni–I distance is 2.481 (2) Å in  $[Ni(ppp)I]^+$ . A somewhat longer Ni–I distance is found in the five-coordinated, distorted square-pyramidal compound  $Ni(psp)I_2$  [psp is  $(C_6H_5)_2P(CH_2)_2S(CH_2)_2P(C_6H_5)_2$ ] (Fälth, 1976) where the Ni–basal I distance is 2.542 (2) Å. A higher coordination number usually means weaker bonds and thus longer bond distances. The Ni–Cl distance in  $[Ni(ppp)Cl]^+$  is 2.169 (3) Å. The average Ni–Cl distance in  $Ni(pop)Cl_2$  [pop is  $(C_6H_5)_2P(CH_2)_2O(CH_2)_2P(C_6H_5)_2$ ] is 2.217 (3) Å (Greene & Sacconi, 1970). Ni in this compound is tetrahedrally coordinated and thus paramagnetic. According to Kilbourn & Powell (1970) the ionic radius of paramagnetic  $Ni^{2+}$  is 0.05 Å greater than that of diamagnetic (square-planar)  $Ni^{2+}$ . The Ni–Cl distances in the two compounds thus correspond very well.

The atoms H(6) and H(22) from different phenyl groups of the ligand molecule are pointing towards the fifth and sixth coordination sites of Ni. The Ni–H(6) distances are 2.80 (1) and 2.78 (1) Å and the Ni–H(22) distances are 2.70 (1) and 2.73 (1) Å for the I and Cl compounds, respectively. These distances are longer than the sum of the van der Waals radii (Pauling, 1960).

As in  $[Ni(ppp)OS(O)CH_3]^+$  the  $X-Ni-P(1)$  and the  $X-Ni-P(3)$  angles ( $X=I$  and  $Cl$ ) are greater than  $90^\circ$  and the  $P(1)-Ni-P(2)$  and the  $P(2)-Ni-P(3)$  angles are smaller than  $90^\circ$ , see Table 2. The distortions of the angles around the Ni atoms are presumably caused by steric strains in the ligand. Scale models predict this also.

The P atoms are  $sp^3$ -hybridized, although in a distorted way. The angles around P vary in  $[Ni(ppp)I]^+$  from 104.5 (5) to 120.9 (6)° and in  $[Ni(ppp)Cl]^+$  from 105.5 (4) to 121.0 (5)°. The corresponding values for  $[Ni(ppp)OS(O)CH_3]^+$  are between 104.8 (6) and 120.6 (4)°. As found in other phosphine ligands (Tolman, 1977) the angles between the substituents of P are less than  $109.5^\circ$ , the only exceptions being C(2)–P(2)–C(3) which are 113.5 (5) and 112.8 (4)° for the I and Cl compounds, respectively. The opening of these C–P–C angles is presumably due to steric strains in the ligand.

The P–C(phenyl) [1.80 (1) Å mean], the P–C(methylene) [1.83 (1) Å mean] and the C–C (of the ligand chain) [1.54 (1) Å mean] distances agree, as well as the angles and distances around B in the  $[B(C_6H_5)_4]^-$  ions (Table 4), with analogous values reported in the literature.

In the first least-squares refinements of the structures the thermal parameters of the atoms C(30), C(31), C(33) and C(34) of one phenyl ring were very large. The peaks in the difference maps of the above atoms were elongated perpendicular to the plane of the phenyl group indicating two alternative positions obtained by a small rotation around an axis through C(29) and C(32) (Fig. 1a and b). A least-squares refinement with two alternative rings C(29A)—C(34A) and C(29B)—C(34B), both with the site occupancy factor 0.5, gave a satisfactory result.

The packing of the molecules is shown in Fig. 3. In the structures there are layers of anions and cations parallel to the (100) planes. The shortest intermolecular distances are I—H(33B) 2.93 (2) Å, Cl—H(33B) 2.73 (1) Å, and the shortest C—H contact between an anion and a cation is 2.62 (1) Å. The H atoms have, however, been generated geometrically.

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## Structures of Pentaammine(5-cyanotetrazolato- $N^2$ )cobalt(III) Perchlorate (CP), [Co(C<sub>2</sub>N<sub>3</sub>)(NH<sub>3</sub>)<sub>5</sub>](ClO<sub>4</sub>)<sub>2</sub>, and (5-Amidinetetrazolato- $N^1, N^5$ )tetraamminecobalt(III) Bromide (ATCB), [Co(C<sub>2</sub>H<sub>3</sub>N<sub>6</sub>)(NH<sub>3</sub>)<sub>4</sub>]Br<sub>2</sub>\*

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**Abstract.** CP:  $M_r = 437.04$ ,  $F(000) = 888$ , monoclinic,  $P2_1/a$ ,  $a = 24.813$  (5),  $b = 7.661$  (2),  $c = 7.971$  (1) Å,  $\beta = 101.17$  (1)°,  $V = 1486.5$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.989$  (2),  $D_x = 1.952$  (1) Mg m<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 1.598$  mm<sup>-1</sup>, room temperature,  $R = 0.081$  on 1937 unique reflections; ATCB:  $M_r = 397.96$ ,  $F(000) = 388$ , triclinic,  $P1$ ,  $a = 7.450$  (6),  $b = 13.471$  (5),  $c = 7.130$  (5) Å,  $\alpha = 96.23$  (6),  $\beta = 117.30$  (7),  $\gamma = 79.51$  (6)°,  $V = 625.0$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.114$  (1),  $D_m = 2.101$  (2) Mg m<sup>-3</sup>, Mo K $\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 7.642$  mm<sup>-1</sup>, room temperature,  $R = 0.049$  on 2120 reflections. Crystals of CP are radiation-sensitive. Both structures determined from Patterson

and Fourier syntheses and refined by least-squares methods. In CP, the Co atom is octahedrally coordinated to ammine groups (1.96–1.99 Å) and a tetrazole-ring N (1.92 Å); in ATCB the Co—ammine distances range in a similar manner (1.95–1.98 Å) while those to the chelate-ring N atoms are 1.91 and 1.94 Å. In CP, one of the perchlorate groups is disordered resulting in a model with five O positions (Cl—O distances: 1.34–1.44 Å) while those for the other ClO<sub>4</sub><sup>-</sup> ion correspond to the expected tetrahedron (1.40–1.44 Å). In both compounds, the coordinated Co-complex ions and the anions form layers. Hydrogen-bonded networks link these anions to the Co<sup>3+</sup> ions *via* the ammine groups.

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**Introduction.** A hot bridgewire is a common method used to ignite a non-primary explosive. In deflagration-

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