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Dibromotris(5-ethyl-5*H*-dibenzophosphole)nickel(II)–2CHCl$_3$

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Abstract. $(C_{14}H_{13}P)_3NiBr_2.(CHCl_3)_2$, M_r = 1094, monoclinic, $a = 16{\cdot}21$ (2), $b = 13{\cdot}03$ (1), $c = 21{\cdot}99$ (2) Å, $\gamma = 92{\cdot}87$ (3)°, $U = 4644$ Å^3, $D_c = 1{\cdot}56$ g cm^{-3}, $Z = 4$, space group $P2_1/n$ $(\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z)$; λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 71·8 cm^{-1}. Hilger & Watts Y920 diffractometer data, 6236 reflexions refined to R = 0·078. The title compound is one of a series of pentacoordinate complexes with the general formula ML_3X_2. The trigonal-bipyramidal geometry is very similar to that of the chloro analogue.

Introduction. The usual solvents for this series of compounds (halobenzene or acetone) having failed to produce usable crystals, solvated dark-green prismatic crystals were obtained in small yield from a 1:1 mixture of chloroform and 2,4-dimethylpentan-3-ol. The specimen (0·3 × 0·3 × 1·0 mm) was mounted in a sealed Lindemann tube. The setting angles of 12 reflexions measured on each side of the incident beam were used in a least-squares calculation to give the cell parameters and orientation matrix. An absorption profile (North, Phillips & Mathews, 1968) was measured for the 020, 040, 060, 080 and 0,12,0 reflexions, and was used to correct the intensities which were measured with an $\omega/2\theta$ scan and a modified ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970). Cu $K\alpha$ radiation was used with Ni/Co balanced filters for $\theta < 20°$, and a Ni β-filter only for $20° < \theta < 60°$. 7360 reflexions were observed, yielding 6236 independent reflexions with $\hat{I} \geq 3\sigma(\hat{I})$. The structure was solved by Patterson methods and refined by a blocked-matrix least-squares method [block 1: scale, dummy isotropic temperature factor (Rollett, 1965), isotropic extinction parameter (Larson, 1970); block 2: chloroform x,y,z; block 3: all other x,y,z; block 4: chloroform anisotropic temperature factors; block 5: all other U_{ii}'s; block 6: all other U_{ij}'s]. H atoms were ignored. Reflexion weights were cal-

Table 1. *Fractional coordinates and estimated standard deviations*

	x	*y*	*z*		*x*	*y*	*z*
C(401)	0·348 (1)	0·307 (1)	0·0109 (7)	C(201)	0·5984 (4)	0·6298 (7)	0·3898 (3)
Cl(401)	0·3805 (3)	0·1889 (4)	0·0311 (2)	C(203)	0·6539 (5)	0·5721 (8)	0·4230 (4)
Cl(402)	0·2451 (2)	0·3000 (3)	−0·0101 (2)	C(204)	0·6787 (5)	0·4786 (8)	0·3986 (4)
Cl(403)	0·5915 (3)	0·6320 (4)	0·0428 (2)	C(205)	0·6507 (5)	0·4416 (7)	0·3445 (4)
C(501)	0·3198 (6)	0·7362 (9)	0·0194 (5)	C(206)	0·5940 (4)	0·4992 (5)	0·3117 (3)
Cl(501)	0·3028 (2)	0·7296 (2)	0·0978 (1)	C(207)	0·5572 (4)	0·4734 (5)	0·2521 (3)
Cl(502)	0·3486 (3)	0·6148 (4)	−0·0063 (2)	C(208)	0·5738 (5)	0·3880 (6)	0·2153 (4)
Cl(503)	0·3907 (3)	0·8340 (5)	0·0022 (2)	C(209)	0·5376 (6)	0·3803 (7)	0·1592 (4)
Br(1)	0·25497 (4)	0·71387 (5)	0·25668 (4)	C(210)	0·4868 (5)	0·4518 (7)	0·1386 (4)
Br(2)	0·35492 (5)	0·69647 (6)	0·43297 (3)	C(211)	0·4666 (5)	0·5354 (6)	0·1747 (3)
Ni(1)	0·37723 (6)	0·68769 (7)	0·32040 (4)	C(212)	0·5041 (4)	0·5455 (5)	0·2309 (3)
P(100)	0·39822 (9)	0·8577 (1)	0·32555 (7)	C(213)	0·5618 (4)	0·7532 (6)	0·2468 (3)
C(101)	0·4257 (4)	0·9364 (5)	0·2588 (3)	C(214)	0·6408 (5)	0·7144 (7)	0·2177 (5)
C(102)	0·3866 (5)	0·9347 (6)	0·2030 (3)	P(300)	0·33206 (9)	0·5241 (1)	0·32769 (7)
C(103)	0·4202 (6)	1·0009 (7)	0·1580 (4)	C(301)	0·3181 (4)	0·4379 (5)	0·2634 (3)
C(104)	0·4890 (6)	1·0656 (7)	0·1685 (4)	C(302)	0·2697 (4)	0·4498 (6)	0·2114 (3)
C(105)	0·5261 (5)	1·0660 (6)	0·2249 (4)	C(303)	0·2623 (5)	0·3689 (7)	0·1700 (3)
C(106)	0·4953 (4)	1·0011 (5)	0·2708 (3)	C(304)	0·3031 (5)	0·2782 (7)	0·1795 (3)
C(107)	0·5276 (4)	0·9919 (5)	0·3322 (3)	C(305)	0·3528 (5)	0·2674 (6)	0·2303 (3)
C(108)	0·5951 (4)	1·0508 (6)	0·3571 (4)	C(306)	0·3594 (4)	0·3467 (5)	0·2731 (3)
C(109)	0·6164 (5)	1·0297 (7)	0·4175 (4)	C(307)	0·4043 (4)	0·3455 (5)	0·3314 (3)
C(110)	0·5762 (5)	0·9553 (7)	0·4525 (4)	C(308)	0·4514 (5)	0·2677 (6)	0·3525 (3)
C(111)	0·5083 (5)	0·8976 (6)	0·4268 (3)	C(309)	0·4887 (5)	0·2759 (6)	0·4100 (3)
C(112)	0·4845 (4)	0·9166 (5)	0·3680 (3)	C(310)	0·4774 (5)	0·3620 (6)	0·4446 (3)
C(113)	0·3063 (4)	0·9163 (5)	0·3566 (4)	C(311)	0·4315 (5)	0·4424 (6)	0·4240 (3)
C(114)	0·3066 (7)	1·0319 (7)	0·3543 (6)	C(312)	0·3957 (4)	0·4329 (5)	0·3665 (3)
P(200)	0·49773 (9)	0·6509 (1)	0·28436 (7)	C(313)	0·2279 (5)	0·5192 (7)	0·3838 (5)
C(202)	0·5689 (4)	0·5928 (6)	0·3351 (3)	C(314)	0·2054 (9)	0·431 (1)	0·3994 (8)

culated from a modified Chebyshev polynomial with three coefficients (Carruthers, 1975). The final *R* was 0·078, and the Hamilton weighted *R* was 0·100.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates are listed in Table 1, and interatomic distances and angles (with estimated standard deviations calculated from the full variance–covariance matrix) in Table 2. Fig. 1 shows the atom numbering.

Table 2. *Interatomic distances* (Å), *interbond angles* (°) *and their e.s.d.'s*

	Molecule (400)	Molelcule (500)
C(1)–Cl(1)	1·72 (2)	1·75 (1)
C(1)–Cl(2)	1·72 (2)	1·76 (1)
C(1)–Cl(3)	1·71 (1)	1·72 (1)

Ni(1)–P(100)	2·228 (2)	Ni(1)–Br(1)	2·466 (2)
Ni(1)–P(200)	2·184 (2)	Ni(1)–Br(2)	2·506 (2)
Ni(1)–P(300)	2·225 (2)		

	Ligand (100)	Ligand (200)	Ligand (300)
P–C(1)	1·833 (7)	1·800 (6)	1·813 (7)
P–(12)	1·820 (7)	1·815 (6)	1·824 (6)
P–(13)	1·841 (6)	1·843 (7)	1·865 (8)
C(1)–C(2)	1·38 (1)	1·37 (1)	1·40 (1)
C(1)–C(6)	1·40 (1)	1·40 (1)	1·41 (1)
C(2)–C(3)	1·41 (1)	1·41 (1)	1·40 (1)
C(3)–C(4)	1·38 (1)	1·41 (1)	1·40 (1)
C(4)–C(5)	1·38 (1)	1·35 (1)	1·39 (1)
C(5)–C(6)	1·39 (1)	1·42 (1)	1·40 (1)
C(6)–C(7)	1·46 (1)	1·47 (1)	1·48 (1)
C(7)–C(8)	1·42 (1)	1·41 (1)	1·38 (1)
C(7)–C(12)	1·41 (1)	1·39 (1)	1·39 (1)
C(8)–C(9)	1·40 (1)	1·37 (1)	1·41 (1)
C(7)–C(10)	1·38 (1)	1·36 (1)	1·38 (1)
C(10)–C(11)	1·42 (1)	1·40 (1)	1·39 (1)
C(11)–C(12)	1·38 (1)	1·38 (1)	1·39 (1)
C(13)–C(14)	1·51 (1)	1·54 (1)	1·42 (1)

	Molecule (400)	Molecule (500)
Cl(1)–C(1)–Cl(2)	111·2 (8)	108·7 (6)
Cl(1)–C(1)–Cl(3)	113·4 (9)	110·6 (6)
Cl(2)–C(1)–Cl(3)	111·9 (9)	113·4 (6)

Br(1)–Ni(1)–P(100)	88·58 (5)
Br(1)–Ni(1)–P(200)	123·96 (5)
Br(1)–Ni(1)–P(300)	86·85 (6)
Br(2)–Ni(1)–P(100)	85·39 (6)
Br(2)–Ni(1)–P(200)	120·09 (5)
Br(2)–Ni(1)–P(300)	86·05 (5)
P(100)–Ni(1)–P(200)	98·21 (7)
P(100)–Ni(1)–P(300)	167·39 (7)
P(200)–Ni(1)–P(300)	94·09 (7)
Br(1)–Ni(1)–Br(2)	115·87 (5)

Table 2 (*cont.*)

	Ligand (100)	Ligand (200)	Ligand (300)
Ni(1)–P(100)–C(101)	122·4 (2)	117·8 (2)	124·2 (2)
Ni(1)–P(100)–C(112)	121·4 (2)	119·1 (2)	119·2 (2)
Ni(1)–P(100)–C(113)	110·2 (2)	118·8 (2)	108·5 (3)
C(101)–P(100)–C(112)		91·2 (3)	91·0 (3)
C(101)–P(100)–C(113)	104·2 (3)	103·4 (3)	103·1 (4)
C(112)–P(100)–C(113)	104·9 (3)	101·9 (3)	108·7 (4)
P(100)–C(101)–C(102)	127·2 (6)	127·9 (6)	128·4 (6)
P(100)–C(101)–C(106)	110·6 (5)	111·0 (5)	110·8 (5)
C(102)–C(101)–C(106)	122·2 (6)	121·0 (6)	120·7 (6)
C(101)–C(102)–C(103)	116·9 (7)	119·3 (8)	118·5 (7)
C(102)–C(103)–C(104)	122·2 (8)	118·9 (8)	120·9 (7)
C(103)–C(104)–C(105)	119·4 (8)	122·6 (7)	120·5 (7)
C(104)–C(105)–C(106)	120·5 (8)	118·3 (8)	119·3 (7)
C(101)–C(106)–C(105)	118·9 (7)	119·9 (7)	119·9 (6)
C(101)–C(106)–C(107)	114·0 (6)	113·2 (6)	113·4 (6)
C(105)–C(106)–C(107)	127·1 (7)	126·9 (6)	126·7 (6)
C(106)–C(107)–C(108)	125·8 (7)	126·9 (6)	126·3 (6)
C(106)–C(107)–C(112)	114·0 (6)	113·8 (6)	113·8 (6)
C(108)–C(107)–C(112)	120·2 (7)	119·3 (7)	119·9 (6)
C(107)–C(108)–C(109)	116·9 (8)	118·5 (8)	119·9 (7)
C(108)–C(109)–C(110)	123·7 (7)	121·8 (8)	119·1 (7)
C(109)–C(110)–C(111)	118·5 (8)	121·0 (8)	122·1 (7)
C(110)–C(111)–C(112)	119·8 (8)	117·9 (8)	117·8 (7)
P(100)–C(112)–C(107)	110·5 (5)	110·8 (5)	110·9 (5)
P(100)–C(112)–C(111)	128·5 (6)	127·6 (6)	127·8 (5)
C(107)–C(112)–C(111)	121·0 (6)	121·5 (6)	121·2 (6)
P(100)–C(113)–C(114)	116·1 (6)	113·4 (6)	117·2 (8)

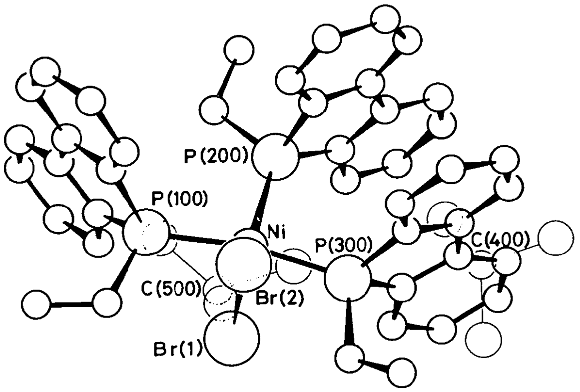

Fig. 1. The title compound projected along **c**.

Discussion. In compounds of the form ML_3X_2, where M = Ni, Pd, Pt; L = 5-alkyl-5*H*-dibenzophosphole (Fig. 1, Powell, Watkin & Wilford, 1971) and X is a halide or pseudohalide, the geometry at the metal atom is determined (Powell & Chui, 1976) by the metal–ligand bond lengths and the interligand non-bonded contacts.

The Ni–Br distance (2·5 Å) lies between the Ni–Cl and Pd–Br lengths, so that the structure of the title compound can be used to help determine the point at which the trigonal bipyramid found in NiL_3Cl$_2$ (Powell & Chui, 1976) becomes unstable and the tetragonal pyramid found in PdL_3Br$_2$ (Chui & Powell, 1974) becomes the preferred geometry. Table 2 shows that

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32547 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Relationships between the interligand bond lengths* (Å) *and angles* (°) *for* $NiCl_2L_3$, $NiBr_2L_3$ *and* $PdBr_2L_3$

	$NiCl_2L_3$	$NiBr_2L_3$	$PdBr_2L_3$
Geometry-independent parameters			
$X(1)–M–L(1)$	86	87	86
$X(1)–M–L(3)$	87	87	87
$L(2)–M–L(1)$	98	98	98
$L(2)–M–L(3)$	95	94	93
$M–X(1)$	2·34	2·47	2·56
$M–L(1)$	2·21	2·23	2·36
$M–L(2)$	2·19	2·18	2·29
$M–L(3)$	2·21	2·23	2·30
Geometry-dependent parameters			
$X(1)–L(1)$	3·11	3·28	3·36
$X(1)–L(3)$	3·14	3·23	3·34
$L(2)–L(1)$	3·33	3·34	3·51
$L(2)–L(3)$	3·24	3·23	3·33
$X(1)–M–L(2)$	127	124	147
$X(1)–M–X(2)$	113	116	103
$X(2)–M–L(2)$	119	120	109
$X(2)–X(1)$	3·92	4·21	4·32
$X(2)–L(2)$	3·92	4·07	4·27
$X(2)–M$	2·35	2·51	2·94

the two Ni—Br bonds are substantially equivalent, and that the geometry is thus very close to that of NiL_3Cl_2. The radial expansion along the metal—halogen bonds may have reduced the ligand—ligand interactions, but not to the extent required to let four of them occupy the essentially planar configuration of the basal ligands in PdL_3Br_2. Table 3 shows that the angles at the metal for the group $MX(1)L(1)L(2)L(3)$ remain constant, independent of changes in the $M–X(1)$ distance [see Powell, Watkin & Wilford (1971) for the definition of $L(1)$ *etc.*]. Increases in the metal—ligand bond lengths are accompanied by an equivalent increase in the ligand—ligand non-bonded contacts, with a consequent preservation of the interbond angles. However, the relaxing interaction between $X(2)$ and both $X(1)$ and $L(2)$ allows these ligands to move away from the trigonal-bipyramidal position and towards the plane perpendicular to the $M–X(2)$ vector, until the geometry ceases to be distorted trigonal bipyramidal and switches over to being distorted tetragonal pyramidal, with a further expansion of the $M–X(2)$ bond to give the normal extended bond found in the tetragonal pyramid.

The dibenzophosphole ligands have their normal form. As is usual in this series of compounds, two are aligned with the major planes parallel to each other, and with their centres of gravity not coinciding in a projection on to the ligand plane. The two molecules of chloroform of solvation are clustered together with their symmetry equivalents about the centre of symmetry at ($\frac{1}{2}$,$\frac{1}{2}$,0). Chloroform (500) is aligned so that the C(501)—H bond is pointing towards Br(2), but the orientation of chloroform (400) does not have any chemical significance. Table 4 shows the relevant intermolecular parameters.

Table 4. *Selected intermolecular parameters*

Br(2)···C(501)	3·56 Å
Br(2)···C(501)···Cl(501)	114·5°
Br(2)···C(501)···Cl(502)	107·5
Br(2)···C(501)···Cl(503)	102·2
C(501)···Br(2)···Ni(1)	131·1

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