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Structures of Bis(1,2-diphenylphosphinoethane)nickel(II) Dinitrate and Bis(cis-1,2-diphenylphosphinoethene)nickel(II) Diperchlorate

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Abstract. [Ni{(C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$}$_2$](NO$_3$)$_2$ (1), $M_r = 979 \cdot 6$, monoclinic, $P2_1/n$, $a = 10 \cdot 430$ (1), $b = 16 \cdot 337$ (2), $c = 13 \cdot 780$ (1) Å, $\beta = 93 \cdot 29$ (1)°, $V = 2344 \cdot 3$ (3) Å^3, $Z = 2$, $D_m = 1 \cdot 37$ (2), $D_x = 1 \cdot 39$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 600$ mm^{-1}, $F(000) = 1020$, room temperature, $R = 0 \cdot 072$ for 1611 reflections. [Ni{(C$_6$H$_5$)$_2$PCHCHP(C$_6$H$_5$)$_2$}$_2$](ClO$_4$)$_2$ (2), $M_r = 1050 \cdot 4$, monoclinic, $P2_1/n$, $a = 14 \cdot 048$ (1), $b = 15 \cdot 994$ (1), $c = 10 \cdot 878$ (1) Å, $\beta = 97 \cdot 08$ (1)°, $V = 2424 \cdot 5$ (5) Å^3, $Z = 2$, $D_m = 1 \cdot 43$ (2), $D_x = 1 \cdot 44$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 695$ mm^{-1}, $F(000) = 1084$, room temperature, $R = 0 \cdot 054$ for 670 reflections. In both compounds the Ni atom lies at a centre of symmetry and is coordinated by two bidentate phosphine ligands in a plane. Slight differences in the structure of the cations arise from the different conformations of the chelate ring. In both compounds the anions are disordered.

Introduction. The two chelating phosphine ligands, (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$ [2-phos, (3)] and the unsaturated analogue *cis*-(C$_6$H$_5$)$_2$PCHCHP(C$_6$H$_5$)$_2$ [2=phos, (4)] are frequently used in coordination chemistry (McAuliffe & Levason, 1979). The chemistry of (3) and (4) is quite similar, but there are a number of significant differences: with cobalt, for example, octahedral complexes [Co(2=phos)$_2$X$_2$]$^+$ are readily formed, whereas the analogous complexes with 2-phos are unstable or may not be prepared (Miskowski, Robbins, Hammond & Gray, 1976). It therefore seemed of interest to study the structures of two closely related complexes of these two ligands in order to investigate

the origins of these differences. The compounds [Ni{(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂}₂](NO₃)₂ (1) and [Ni{(C₆H₅)₂PCHCHP(C₆H₅)₂}₂](ClO₄)₂ (2) offered a suitable possibility for comparison. The syntheses of these compounds have been reported (Hudson, Nyholm & Stiddard, 1968; McAuliffe & Meek, 1969), but the structures have not been determined.

Experimental. Preparation of crystals: (1) by mixing hot ethanolic solutions of Ni(NO₃)₂.6H₂O and 2-phos in stoichiometric ratio 1:2. On cooling, fine yellow crystals deposited. An attempted synthesis of [Ni-{(C₆H₅)₂PCHCHP(C₆H₅)₂}₂](NO₃)₂ by this method gave a yellow powder which was insoluble in all solvents tried. Compound (2) from nickel(II) perchlorate hexahydrate and 2=phos as for (1), giving a fine yellow powder. Small yellow crystals of quality suitable for X-ray diffraction obtained by slow evaporation of an acetonitrile solution. Density measured by flotation.

Size of crystals used: (1) 0·27 × 0·13 × 0·13 mm and (2) 0·10 × 0·08 × 0·04 mm. Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan, room temperature. When the first scan of a reflection showed it to be weak, the reflection was skipped; otherwise the reflection was scanned repeatedly to a maximum of four scans for (1) and six scans for (2) or until a preset number of counts [3000 for (1), 4000 for (2)] was attained. Three standard reflections measured every 100 min showed variations of less than $2\cdot5\sigma(I)$ and no correction for change in intensity was applied. Details of the measurements are given in Table 1. Data corrected for Lorentz and polarization effects but not for absorption or extinction. Heavy-atom methods. All calculations used a local version of XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) or ORTEPII (Johnson, 1976). Scattering factors for neutral atoms from Cromer & Mann (1968), and anomalous-dispersion corrections for Fe, P and Cl from International Tables for X-ray Crystallography (1974). H atoms in calculated positions.

Discussion. Atomic coordinates and equivalent isotropic temperature factors are given in Table 2 for (1) and Table 3 for (2). Table 4 gives selected bond lengths and bond angles.* Fig. 1 shows the atomic numbering of the asymmetric unit of the cations, and Fig. 2 gives a view of the cation projected onto the NiP₄ plane.

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* Lists of structure factors, atomic positional and anisotropic displacement parameters for atoms, and other information in the printed form of the Standard Crystallographic File Structure of Brown (1985) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51728 (63 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental data for* (1) *and* (2)

	(1)	(2)
Determination of cell dimensions		
No. of reflections	27	31
2θ range (°)	28–45	20–39
Intensity measurements		
Scan speed (° s⁻¹)	0·10	0·10
Scan width (°)	1·5 + 0·3tanθ	1·0 + 0·2tanθ
2θ range (°)	6–50	6–50
hkl limits	0 < h ≤ 11, 0 ≤ k ≤ 18, −16 ≤ l ≤ 16	0 < h ≤ 14, 0 ≤ k ≤ 17, −12 ≤ l ≤ 10
Total reflections	2261	864
Unique reflections	2153	838
Observed [$I > 3\sigma(I)$]	1611	670
R_{int}	0·018	0·036
Refinement	$|F|$, full-matrix	$|F|$, full-matrix
Atoms anisotropic	Fe, P, C(1), C(2)	Fe, P
Weights	Unit	Unit
R	0·072	0·054
S	2·64	1·48
Variables/reflections	168/1611	155/670
$(\Delta/\sigma)_{max}, (\Delta/\sigma)_s$,	0·315, 0·028	0·76, 0·054
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$(e Å⁻³)	+0·70, −0·47	+0·34, −0·36

Table 2. *Fractional coordinates, isotropic (or equivalent isotropic) atomic displacement factors* U (Å² × 10³) *and population parameters PP for compound* (1)

$$U_{eq} = \tfrac{1}{3}\Sigma_i U_{ii}.$$

	x	y	z	U	PP
Ni	0	0	0	28·2 (6)	
P(1)	0·0459 (3)	−0·12441 (20)	−0·0609 (3)	51·3 (12)	
P(2)	0·21249 (22)	0·0023 (3)	0·04120 (20)	43·9 (10)	
O(1)	0·1778 (17)	0·0722 (11)	0·7581 (14)	79 (8)	0·535 (24)
O(2)	0·181 (3)	0·1552 (24)	0·657 (3)	169 (13)	0·535
O(3)	0·273 (5)	0·058 (3)	0·613 (4)	233 (20)	0·535
O(101)	0·176 (4)	0·0931 (25)	0·601 (3)	156 (15)	0·465
O(102)	0·2999 (24)	0·0397 (16)	0·7243 (19)	98 (10)	0·465
O(103)	0·269 (4)	0·1741 (25)	0·707 (3)	161 (15)	0·465
N	0·2294 (16)	0·0963 (11)	0·6895 (12)	96 (4)	
C(1)	0·2235 (11)	−0·1353 (10)	−0·0626 (13)	99 (7)	
C(2)	0·2927 (11)	−0·0660 (9)	−0·0426 (10)	70 (6)	
C(11)	−0·0024 (13)	−0·2135 (7)	0·0105 (10)	52 (3)	
C(12)	0·0535 (13)	−0·2905 (9)	−0·0175 (10)	68 (4)	
C(13)	0·0225 (14)	−0·3584 (10)	0·0368 (11)	83 (5)	
C(14)	−0·0572 (14)	−0·3534 (10)	0·1107 (11)	85 (5)	
C(15)	−0·1068 (14)	−0·2776 (10)	0·1363 (11)	83 (5)	
C(16)	−0·0737 (12)	−0·2091 (8)	0·0850 (10)	63 (4)	
C(21)	0·2381 (11)	−0·0420 (7)	0·1599 (8)	49 (3)	
C(22)	0·3614 (12)	−0·0546 (8)	0·2008 (10)	63 (4)	
C(23)	0·3770 (15)	−0·0862 (10)	0·2933 (12)	84 (5)	
C(24)	0·2718 (15)	−0·1033 (10)	0·3483 (11)	88 (5)	
C(25)	0·1480 (14)	−0·0952 (9)	0·3044 (10)	75 (4)	
C(26)	0·1328 (11)	−0·0634 (8)	0·2107 (9)	55 (3)	
C(31)	−0·0159 (11)	−0·1400 (7)	−0·1861 (8)	51 (3)	
C(32)	0·0361 (16)	−0·0957 (11)	−0·2604 (13)	98 (5)	
C(33)	−0·0204 (18)	−0·1007 (12)	−0·3524 (14)	109 (6)	
C(34)	−0·1242 (15)	−0·1479 (10)	−0·3710 (12)	88 (5)	
C(35)	−0·1708 (13)	−0·1981 (9)	−0·3032 (10)	71 (4)	
C(36)	−0·1170 (11)	−0·1928 (8)	−0·2062 (9)	53 (3)	
C(41)	0·3144 (10)	0·0916 (7)	0·0412 (8)	40 (3)	
C(42)	0·3630 (10)	0·1274 (7)	0·1270 (8)	44 (3)	
C(43)	0·4390 (11)	0·1979 (8)	0·1213 (9)	52 (3)	
C(44)	0·4706 (11)	0·2312 (8)	0·0358 (9)	57 (3)	
C(45)	0·4251 (12)	0·1948 (8)	−0·0490 (9)	60 (3)	
C(46)	0·3494 (11)	0·1256 (8)	−0·0478 (8)	52 (3)	

Both structures contain centrosymmetric [NiL₂]²⁺ cations with disordered anions. In (1) the disorder was modelled as two nitrate anions with a common nitrogen position. The population parameters of the three O atoms of each nitrate were constrained to be equal, and the sum of the populations of the two sites constrained to be 1. The refinement gave populations for the two

Table 3. *Fractional coordinates, isotropic (or equivalent isotropic) atomic displacement factors* U ($\text{Å}^2 \times 10^3$) *and population parameters PP for compound* (2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i U_{ii}$$

	x	y	z	U	PP
Ni	0	0	0	29·6 (16)	
Cl	0·1675 (6)	0·4074 (5)	−0·2678 (8)	71·0 (23)	
P(1)	0·0582 (4)	0·1287 (4)	−0·0343 (5)	31·1 (21)	
P(2)	−0·0559 (4)	0·0045 (5)	−0·2037 (5)	32·9 (22)	
O(1)	0·2431 (17)	0·4264 (15)	−0·3377 (21)	124	
O(2)	0·098 (3)	0·374 (4)	−0·358 (5)	124	0·5
O(3)	0·106 (4)	0·449 (3)	−0·197 (5)	124	0·5
O(4)	0·202 (3)	0·338 (3)	−0·178 (5)	124	0·5
O(5)	0·151 (4)	0·324 (3)	−0·279 (5)	124	0·5
O(6)	0·092 (4)	0·456 (3)	−0·330 (5)	124	0·5
O(7)	0·203 (4)	0·447 (3)	−0·165 (5)	124	0·5
C(1)	0·0616 (16)	0·1398 (15)	−0·1984 (20)	42 (6)	
C(2)	0·0110 (16)	0·0865 (14)	−0·2703 (20)	36 (6)	
C(11)	−0·0134 (19)	0·2144 (13)	0·0013 (24)	39 (6)	
C(12)	0·0019 (16)	0·2943 (14)	−0·0442 (18)	38 (7)	
C(13)	−0·0559 (16)	0·3601 (16)	−0·0164 (21)	50 (7)	
C(14)	−0·1282 (17)	0·3489 (17)	0·0536 (22)	59 (8)	
C(15)	−0·1450 (18)	0·2738 (17)	0·0996 (22)	54 (7)	
C(16)	−0·0883 (18)	0·2040 (16)	0·0680 (21)	46 (7)	
C(21)	−0·1788 (16)	0·0364 (14)	−0·2287 (23)	48 (7)	
C(22)	−0·2246 (18)	0·0440 (14)	−0·3513 (22)	46 (7)	
C(23)	−0·3225 (20)	0·0682 (16)	−0·3696 (22)	50 (7)	
C(24)	−0·3697 (20)	0·0847 (18)	−0·271 (3)	69 (9)	
C(25)	−0·3222 (19)	0·0825 (17)	−0·149 (3)	62 (8)	
C(26)	−0·2265 (17)	0·0570 (14)	−0·1320 (20)	35 (6)	
C(31)	0·1798 (13)	0·1534 (12)	0·0297 (18)	25 (5)	
C(32)	0·2540 (18)	0·1102 (16)	−0·0155 (22)	56 (7)	
C(33)	0·3492 (18)	0·1250 (17)	0·0436 (23)	61 (8)	
C(34)	0·3662 (18)	0·1764 (16)	0·1390 (23)	56 (8)	
C(35)	0·2931 (19)	0·2203 (17)	0·1799 (22)	57 (8)	
C(36)	0·1996 (17)	0·2116 (16)	0·1272 (22)	48 (7)	
C(41)	−0·0442 (15)	−0·0833 (13)	−0·3049 (18)	29 (6)	
C(42)	−0·1222 (15)	−0·1333 (14)	−0·3534 (19)	40 (6)	
C(43)	−0·1110 (17)	−0·1996 (15)	−0·4303 (20)	46 (7)	
C(44)	−0·0196 (17)	−0·2190 (15)	−0·4538 (20)	48 (7)	
C(45)	0·0579 (16)	−0·1746 (14)	−0·4101 (21)	45 (7)	
C(46)	0·0472 (16)	−0·1028 (16)	−0·3382 (21)	52 (7)	

sites, of 54(3) and 46(3)% respectively, with reasonable N—O bond distances and angles. In (2) the anion was modelled as two perchlorates with a population of 50%, and common Cl and O(1) positions [*i.e.* a rotational disorder about the Cl—O(1) bond].

The structures of the cations show a number of common features which are discussed before the differences. In both cases the centre of symmetry requires the coordination of the Ni atom by the four P atoms to be planar, and, with P(1)—Ni—P(2) bite angles of 83·25 (12) and 84·2 (2)° for (1) and (2) respectively, the coordination is very close to ideal square planar, as expected for a low-spin d^8 complex. The d^8 character of the nickel is nicely illustrated by the fact that (2) may be crystallized from acetonitrile without solvent of crystallization, whereas the d^6 iron(II) system crystallizes from the same solvent with two acetonitrile molecules completing the octahedral coordination sphere of the iron to give [Fe(2=phos)₂(CH₃CN)₂]-(ClO₄)₂ (5) (Williams, 1988). The Ni—P distances are identical within experimental error, and are 0·06 (1) Å shorter than the Fe—P distance in (5). This shortening is presumably responsible for the slightly larger bite angle in (1) and (2) than in (5) [82·57 (9)°]. The least-squares plane defined by P(1), P(2), C(1) and C(2)

Table 4. *Selected bond lengths* (Å) *and angles* (°) *for* (1) *and* (2)

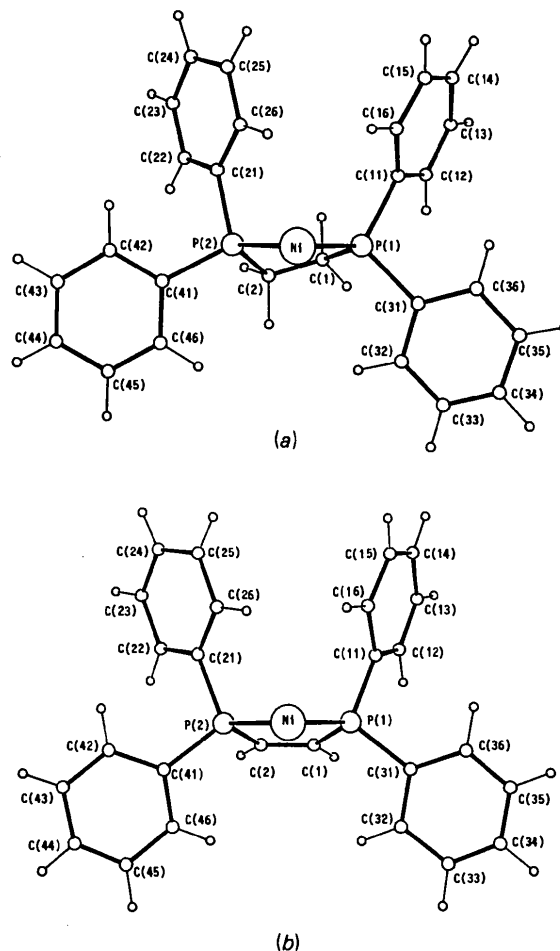|	(1)	(2)
Ni–P(1)	2·261 (3)	2·264 (6)
Ni–P(2)	2·256 (3)	2·258 (5)
P(1)–C(1)	1·862 (12)	1·80 (2)
P(1)–C(11)	1·843 (13)	1·77 (2)
P(1)–C(31)	1·825 (12)	1·81 (2)
P(2)–C(2)	1·841 (14)	1·82 (2)
P(2)–C(21)	1·794 (12)	1·79 (2)
P(2)–C(41)	1·804 (12)	1·80 (2)
C(1)–C(2)	1·36 (2)	1·31 (3)
Ni–P(1)–C(1)	108·8 (5)	107·8 (8)
Ni–P(1)–C(11)	116·2 (4)	116·2 (9)
Ni–P(1)–C(31)	113·9 (4)	118·6 (7)
Ni–P(2)–C(2)	107·9 (4)	106·2 (7)
Ni–P(2)–C(21)	108·4 (4)	111·7 (9)
Ni–P(2)–C(41)	125·7 (4)	121·8 (7)
C(1)–P(1)–C(11)	103·5 (7)	103·1 (12)
C(1)–P(1)–C(31)	105·8 (7)	102·8 (10)
C(11)–P(1)–C(31)	107·6 (6)	106·4 (11)
C(2)–P(2)–C(21)	106·1 (6)	105·7 (11)
C(2)–P(2)–C(41)	101·6 (5)	103·2 (10)
C(21)–P(2)–P(41)	105·6 (5)	106·8 (10)
P(1)–C(1)–C(2)	115·7 (11)	116·8 (18)
P(2)–C(2)–C(1)	112·1 (10)	120·2 (18)
P(1)–C(1)–C(2)–P(2)	30·82 (15)	−1·5 (2·7)

(a)

(b)

Fig. 1. The asymmetric units of the cations (a) [Ni(Ph₂PCH₂CH₂PPh₂)₂]²⁺ and (b) [Ni(Ph₂PCHCHPPh₂)₂]²⁺ showing the atomic numbering. The anions have been omitted.

is inclined at 19·7 (5) (1) and 19·9 (5)° (2) to the NiP_4 coordination plane, and this allows the phenyl rings to be distinguished as axial (rings 1 and 2) with the twofold axis of the phenyl ring nearly perpendicular to the NiP_4 plane, or as equatorial (rings 3 and 4) with the twofold axis lying closer to the NiP_4 plane. In both compounds the axial phenyls are turned so as to be roughly parallel to the Ni—P bond (Fig. 2), and the equatorial phenyls are turned so as to be roughly parallel to a plane bisecting the complex between the two ligands. This results in one short non-bonded intramolecular distance between the equatorial phenyls $[C(36)\cdots C(42)(-x, -y, -z) = 3\cdot04$ (2) (1), $3\cdot08$ (3) Å (2)], and one short non-bonded axial-equatorial distance $[(1) C(16)\cdots C(46)(-x, -y, -z) = 3\cdot20$ (2) Å; (2) $C(26)\cdots C(32)(-x, -y, -z) = 3\cdot17$ (3) Å].

In discussing the differences between the two structures it is convenient to begin with (2), and to note that the cation has an approximate non-crystallographic mirror plane bisecting the asymmetric unit through the Ni atom and the mid-point of the C(1)—C(2) bond (Fig. 1b). In agreement with this, and as expected for a C—C double bond, the dihedral angle P(1)—C(1)—C(2)—P(2) is very close to zero [1·5 (2·7)°]; in the octahedral iron(II) complex (5) of ligand (4) this mirror plane is indeed present as part of the crystallographic symmetry.

If the C—C double bond in ligand (4) were replaced by a C—C single bond as in (3), one would expect the C(1)—C(2) distance to increase, and the dihedral angle P(1)—C(1)—C(2)—P(2) to open towards the ideal value of 60°. The structure of (1) may be obtained from that of (2) by twisting the ligand about the mid-point of the bond C(1)—C(2) while keeping the phosphorus positions fixed: the C(1)—C(2) bond lengthens and the dihedral angle opens. C(1) moves closer to the NiP_4 plane and C(2) moves away from it; rings 2 and 3 are moved towards an axial position, and rings 1 and 4 move towards an equatorial position. The dihedral angle P(1)—C(1)—C(2)—P(2) in (1) is 30·82 (15)°. This conformation is essentially the same as that reported for $[Rh(2\text{-}phos)_2](ClO_4)$ (Hall, Kilbourn & Taylor, 1970). The result of this twisting is that ring 2 is tilted in towards the Ni atom, and will thereby give a greater hindrance to any attack perpendicular to the NiP_4 plane.

In conclusion, the very similar Ni—P bond distances and bite angles for (1) and (2) suggest that the differences between ligands (3) and (4) do not arise from any major electronic effect. On the other hand, the twisting of the ligand arising from the conformation of the chelate ring in (1) could give rise to steric hindrance of the coordination site cis to the bidentate phosphine ligand. Such a possibility was proposed by McAuliffe & Meek (1969) on the basis of molecular models; the structures presented in this paper support this hypothesis, and suggest that the differences between the two ligands may be attributed to the greater steric hindrance of (3).
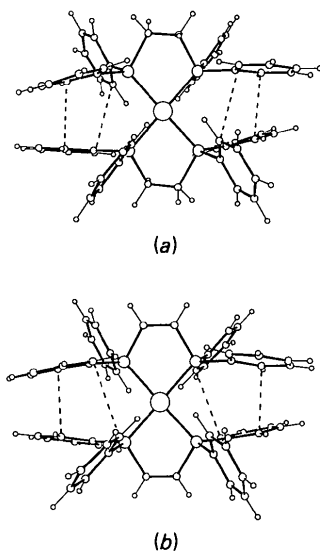
(a)

(b)

Fig. 2. View of the cations in (a) (1) and (b) (2) perpendicular to the NiP_4 plane. The dashed lines show intramolecular distances < 3·2 Å.

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