Discussion. The Fe atom occupies a special position (2*a*) of space group *Imm*2, thus the $[Fe(CN)_6]^{4-}$ unit has *mm*2 symmetry. The Li ions also lie in special positions, (4*c*) and (4*d*), and one of the oxygen atoms, O(2), of the coordination water molecules also occupies a special position (2*b*); therefore the hydrated cation $[Li_4(OH_2)_5]^{4+}$ also possesses *mm*2 symmetry. However, the HMT molecule only shows *m* symmetry; the atoms C(13), C(14) N(12) and N(13) lie in special positions (4*c*).

Both compounds $Li_n[Fe(CN)_6].2C_6H_{12}N_4.5H_2O$ (n = 3,4) may be regarded as a body-centred $[Fe(CN)_6]^{n-}$ packing containing HMT molecules in tetrahedral interstices and $[Li_n(OH_2)_5]^{n+}$ ions in octahedral interstices.

The two compounds can be distinguished by structure analysis, by IR ν(C≡N) stretching frequencies (2115, 2014 cm^{-1} for Fe^{3+}, Fe^{2+} respectively) and by their Mössbauer spectra: the Fe^{2+} compound gives an undistorted singlet whereas the Fe^{3+} compound, which contains disordered Li ions, gives two doublets.

The structure is stabilized by hydrogen bonds between water molecules and N atoms N(11), N(13) and N(1), which are not coordinated to Li atoms. The mean O—H···N distance is 2·90 Å.

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Diiodobis(triphenylphosphine)nickel(II)

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Abstract. $[NiI_2(C_{18}H_{15}P)_2]$, $M_r = 837\cdot09$, monoclinic, $P2_1/c$, $a = 19\cdot361\ (17)$, $b = 10\cdot220\ (5)$, $c = 17\cdot995\ (13)$ Å, $\beta = 112\cdot26\ (7)°$, $V = 3296\ (3)$ Å^3, $Z = 4$, $D_x = 1\cdot687$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 2\cdot56$ mm^{-1}, $F(000) = 1640$, $T = 291$ K, $R = 0\cdot0780$ for 4302 independent observed reflections. The nickel atom has a distorted tetrahedral geometry, angles subtended at the metal ranging from 103·40 (9) to 118·12 (6)°. Average Ni—I and Ni—P distances are 2·5307 (25) and 2·382 (4) Å, respectively.

Introduction. Dihalogenobisphosphine complexes of the nickel triad are exceptionally well known species, frequently being cited as classic examples of tetrahedral (Ni) or square-planar (Ni, Pd, Pt) transition-metal complexes (and, for certain of the nickel species, examples of facile interconversion between structural isomers).

One of our ongoing interests is the application of molecular-orbital (MO) methods in transition-metal chemistry, one aspect of which concerns the reproducibility of results derived from MO calculations performed at differing levels of sophistication. We considered that the series of molecules $X_2Ni(PR_3)_2$ would represent suitable species for comparative MO calculations, since they are relatively simple, have variable geometries, and contain both π-donor and π-acceptor ligands. However, we were very surprised to discover that no precise structural data (the starting point for these calculations) on any iodide was available in the literature. Accordingly, we herein present the derived molecular parameters of $I_2Ni(PPh_3)_2$.

Experimental. Compound prepared according to the literature (Venanzi, 1958), and purity checked by microanalysis; relatively poor quality black plates

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Table 1. *Coordinates of refined atoms and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0·76058 (8)	0·12720 (13)	0·06910 (8)	0·0549 (9)
I(1)	0·89090 (5)	0·21965 (8)	0·10601 (5)	0·0684 (6)
I(2)	0·65781 (6)	0·28112 (10)	0·06716 (6)	0·1056 (9)
P(1)	0·77829 (14)	−0·0469 (3)	0·15901 (15)	0·0457 (17)
P(2)	0·72672 (15)	0·0266 (3)	−0·06189 (17)	0·0501 (18)
C(112)	0·6285 (4)	−0·0635 (6)	0·1339 (5)	0·075 (9)
C(113)	0·5629	−0·1255	0·1295	0·097 (12)
C(114)	0·5642	−0·2572	0·1502	0·100 (13)
C(115)	0·6311	−0·3269	0·1752	0·087 (11)
C(116)	0·6967	−0·2649	0·1795	0·072 (9)
C(111)	0·6954	−0·1332	0·1589	0·046 (6)
C(122)	0·9159 (4)	−0·1513 (5)	0·1781 (4)	0·053 (7)
C(123)	0·9646	−0·2440	0·1681	0·063 (8)
C(124)	0·9364	−0·3577	0·1243	0·074 (9)
C(125)	0·8595	−0·3787	0·0904	0·074 (9)
C(126)	0·8108	−0·2860	0·1004	0·054 (7)
C(121)	0·8390	−0·1723	0·1442	0·045 (6)
C(132)	0·8584 (4)	−0·1036 (4)	0·3220 (4)	0·060 (8)
C(133)	0·8936	−0·0717	0·4032	0·072 (9)
C(134)	0·8968	0·0583	0·4278	0·057 (7)
C(135)	0·8648	0·1564	0·3713	0·067 (9)
C(136)	0·8296	0·1245	0·2901	0·055 (7)
C(131)	0·8264	−0·0054	0·2655	0·043 (6)
C(212)	0·5944 (4)	0·0630 (5)	−0·1974 (4)	0·055 (7)
C(213)	0·5460	0·1383	−0·2603	0·075 (9)
C(214)	0·5605	0·2709	−0·2654	0·071 (9)
C(215)	0·6233	0·3283	−0·2076	0·077 (9)
C(216)	0·6717	0·2531	−0·1447	0·067 (8)
C(211)	0·6572	0·1204	−0·1396	0·047 (7)
C(222)	0·7872 (3)	0·0318 (6)	−0·1818 (4)	0·053 (7)
C(223)	0·8434	0·0080	−0·2109	0·073 (9)
C(224)	0·9119	−0·0428	−0·1599	0·072 (9)
C(225)	0·9241	−0·0698	−0·0799	0·076 (9)
C(226)	0·8679	−0·0461	−0·0508	0·062 (8)
C(221)	0·7995	0·0047	−0·1018	0·049 (7)
C(232)	0·6271 (4)	−0·1517 (8)	−0·0444 (4)	0·060 (8)
C(233)	0·5983	−0·2764	−0·0430	0·076 (9)
C(234)	0·6278	−0·3841	−0·0684	0·088 (11)
C(235)	0·6860	−0·3673	−0·0953	0·084 (10)
C(236)	0·7148	−0·2426	−0·0967	0·063 (8)
C(231)	0·6854	−0·1349	−0·0712	0·047 (7)

Table 2. *Internuclear distances* (Å) *and interbond angles* (°)

Ni—I(1)	2·5352 (17)	P(1)—C(121)	1·825 (7)
Ni—I(2)	2·5261 (18)	P(1)—C(131)	1·835 (7)
Ni—P(1)	2·341 (3)	P(2)—C(211)	1·806 (7)
Ni—P(2)	2·422 (3)	P(2)—C(221)	1·819 (7)
P(1)—C(111)	1·830 (8)	P(2)—C(231)	1·815 (8)

I(1)—Ni—I(2)	118·12 (6)	C(211)—P(2)—C(221)	102·8 (3)
I(1)—Ni—P(2)	103·40 (9)	C(211)—P(2)—C(231)	103·8 (4)
I(1)—Ni—P(2)	106·79 (9)	C(221)—P(2)—C(231)	103·4 (3)
I(2)—Ni—P(1)	113·07 (9)	P(1)—C(111)—C(112)	117·4 (6)
I(2)—Ni—P(2)	109·23 (9)	P(1)—C(111)—C(116)	122·6 (6)
P(1)—Ni—P(2)	105·30 (11)	P(1)—C(121)—C(122)	117·9 (5)
Ni—P(1)—C(111)	117·8 (3)	P(1)—C(121)—C(126)	122·1 (5)
Ni—P(1)—C(121)	111·55 (24)	P(1)—C(131)—C(132)	120·3 (5)
Ni—P(1)—C(131)	115·42 (24)	P(1)—C(131)—C(136)	119·7 (5)
C(111)—P(1)—C(121)	105·9 (3)	P(2)—C(211)—C(212)	122·5 (5)
C(111)—P(1)—C(131)	102·2 (3)	P(2)—C(211)—C(216)	117·3 (5)
C(121)—P(1)—C(131)	102·4 (3)	P(2)—C(221)—C(222)	121·8 (5)
Ni—P(2)—C(211)	112·1 (3)	P(2)—C(221)—C(226)	118·1 (5)
Ni—P(2)—C(221)	118·08 (25)	P(2)—C(231)—C(232)	117·8 (6)
Ni—P(2)—C(231)	115·1 (3)	P(2)—C(231)—C(236)	121·9 (6)

grown from CH_2Cl_2 solution at 243 K; crystal selected, *ca* 0·4 × 0·3 × 0·1 mm, mounted on glass fibre and set on Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$ X-radiation, graphite monochromator); cell parameters and orientation matrix from least-squares refinement of θ values ($13 < \theta < 15°$) of 25 centred reflections; data collected by ω–2θ scans in 96 steps with ω scan width $(0{\cdot}8 + 0{\cdot}34\tan\theta)°$; data ($h$: 0 to 23, k: 0 to 12, l: −21 to 21) measured for $1 \le \theta \le 25°$ over 94 X-ray hours; no detectable crystal decay or movement; corrections for Lorentz and polarization effects (Gould & Smith, 1986), and, following isotropic convergence, for absorption (Walker & Stuart, 1983), affording correction factors ranging from 0·74–1·13; 6310 reflections measured, 4445 [$F \ge 2{\cdot}0\sigma(F)$] retained, of which 4302 are unique ($R_{int} = 0{\cdot}016$); structure solution *via* automatic direct methods (Sheldrick, 1986) for Ni, P, and I atoms, and iterative full-matrix least-squares refinement (on F)/ΔF syntheses (Sheldrick, 1976), for C atoms; weights assigned according to $w^{-1} = [\sigma^2(F) + 0{\cdot}000291F^2]$; phenyl groups treated as regular, planar hexagons (C—C 1·395 Å) with idealized, riding H atoms (C—H 1·08 Å); non-H atoms refined anisotropically, H atoms sharing an overall isotropic thermal parameter, 0·086 (7) Å^2 at convergence; 299 variable parameters, data:variable ratio > 14:1; $R = 0{\cdot}0780$, $wR = 0{\cdot}0879$, $S = 1{\cdot}527$; max. shift/e.s.d. in final cycle 0·088; max. and min. residues in final ΔF synthesis 1·42 and −1·37 e Å^{-3} (near iodine positions); scattering factors for P, C, and H inlaid in *SHELX*76; scattering factors for Ni and I from *International Tables for X-ray Crystallography* (1974); figure drawn using *EASYORTEP* (Mallinson, 1982); molecular geometry calculated by *CALC* (Gould & Taylor, 1986); all calculations performed on an Amdahl 470 V/8 computer.

Discussion. The unit-cell dimensions previously reported for this compound [Garton, Henn, Powell & Venanzi (GHPV) (1963)] have been confirmed, but the correct space group is $P2_1/c$ and not either Pc or $P2/c$. Table 1* lists the coordinates of refined atoms and equivalent isotropic thermal parameters, whilst Table 2 details the internuclear distances and interbond angles determined. A perspective view of a single molecule is shown in Fig. 1.

The compound crystallizes with no important contacts between adjacent molecules. The geometry at nickel is clearly distorted tetrahedral, angles varying from 103·40 (9) [I(1)—Ni—P(1)] to 118·12 (6)° [I—Ni—I]. The P—Ni—P angle is 105·30 (11)°. This continues a smooth decrease from 116·6° in $Cl_2Ni(PPh_3)_2$ (GHPV, 1963), and 110·4 (2)° in $Br_2Ni(PPh_3)_2$ (Jarvis, Mais & Owston, 1968). However, it is not the case that as P—Ni—P decreases, X—Ni—X increases along the same series. In the dichloride the

* Lists of structure factors, H-atom positions, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51132 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

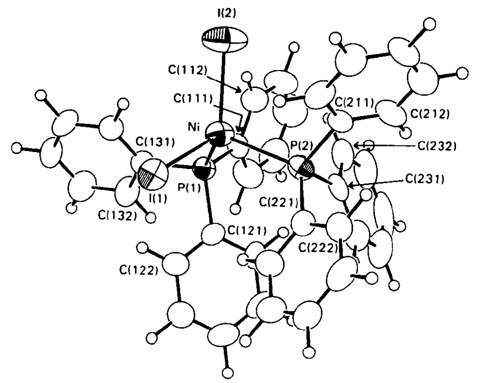

Fig. 1. Perspective view of $I_2Ni(PPh_3)_2$ (50% thermal ellipsoids). The numbering of C atoms in the phenyl rings is cyclic, C(*ijk*), where *i* is the number of the attached phosphorus, $j = 1$–3, and $k = 1$–6. H atoms, which have been given an artificial radius of 0·1 Å for clarity, carry the same number as the C atom to which they are attached.

latter angle is 123·3°, in the dibromide 126·3 (1)°, and in the diiodide herein, only 118·12 (6)°. In fact, in terms of the root-mean-square distortion (r.m.s.d.) of the angles at nickel from the tetrahedral ideal, the diiodide (r.m.s.d. 4·99°) is the least distorted molecule, the dichloride intermediate (r.m.s.d. 7·56°), and the dibromide the most distorted (r.m.s.d. 8·10°). These results emphasize the dangers of the assumption of simple structural patterns in a series of seemingly innocuous analogues. Since none of the three compounds are pairwise isomorphous it is certainly possible that differing intramolecular steric requirements of the triphenylphosphine ligands are at least partially responsible for the observed angles at nickel, but we have not pursued this possibility in any detail.

The Ni—I distances in $I_2Ni(PPh_3)_2$ are barely different, average 2·5307 (25) Å. In contrast, Ni—P(2) is longer than Ni—P(1) by 0·081 (4) Å, the average Ni—P distance being 2·382 (4) Å. This is longer than that observed in the dichloride (2·28 Å) and the dibromide (2·333 Å), a trend that can readily be correlated with the decreasing π-donor capability of the heavier halides. On the other hand, the changes in the average Ni—X distance [dichloride to dibromide, 0·07 Å (less than the difference in covalent radii), and dibromide to diiodide, 0·19 Å (exactly the difference in covalent radii)] do not easily fit with this pattern. A case could be made for a redetermination of $Cl_2Ni(PPh_3)_2$, for which only a rather inaccurate two-dimensional study is currently available (GHPV, 1963).

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Structure of Aqua[*N,N'*-bis(*β*-carbamoylethyl)-*trans*-1,2-cyclohexanediamine]copper(II) Perchlorate*

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Abstract. $[Cu(C_{12}H_{24}N_4O_2)(H_2O)](ClO_4)_2$, $M_r = 536{\cdot}81$, monoclinic, $P2_1/c$, $a = 15{\cdot}445$ (3), $b = 11{\cdot}412$ (2), $c = 13{\cdot}745$ (3) Å, $\beta = 116{\cdot}12$ (2)°, $V = 2175{\cdot}5$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}639$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 12·54 cm^{-1}, $F(000) = 1108$, $R = 0{\cdot}054$, $wR = 0{\cdot}059$ for 2612 independent reflections at room temperature. The copper(II) ion is in a slightly distorted square pyramid with the diaminodiamide equatorial and the O atom of the aqua group axial. The perchlorate anions are disordered in the lattice.

* Aqua(3-{2-[(2-carbamoylethyl)amino]cyclohexylamino}propionamide)copper(II) diperchlorate.

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