new unsymmetrical EPT donor. The small size of the crystals obtained by electrocrystallization precluded resisitivity measurements using the four-probe technique. However, preliminary two-probe measurements indicate that the product described here is semiconducting. The dimerization of the EPT donor cations in this structure probably leads to localization of charge and, as a result, metallic conductivity is not expected.

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Structure of the Adduct Lithium Hexacyanoferrate(II)–Hexamethylenetetramine–Water (1/2/5)

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Abstract. $Li_4[Fe(CN)_6].2C_6H_{12}N_4.5H_2O$, $M_r = 610{\cdot}2$, orthorhombic, $Imm2$, $Z = 2$, $a = 14{\cdot}849\,(3)$, $b = 10{\cdot}393\,(3)$, $c = 9{\cdot}098\,(3)$ Å, $V = 1404\,(3)$ Å^3, $D_x = 1{\cdot}44$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}4$ cm^{-1}, $F(000) = 436$, room temperature, final $R = 0{\cdot}040$ for 729 unique reflections and 129 variables. The structure consists of a body-centred arrangement of $[Fe(CN)_6]^{4-}$ octahedra, $C_6H_{12}N_4$ molecules which occupy the tetrahedral interstices, and $[Li_4(OH_2)_5]^{4+}$ units, which occupy the octahedral interstices. The Li ions are further connected by Li—N contacts to the hexamethylene tetramine molecules and hexacyanoferrate groups.

Introduction. The crystal structures of addition compounds of metal hexacyanoferrates with hexamethylenetetramine (HMT) (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) investigated so far show comparable building patterns (Meyer & Pickardt, 1988). The structures may be thought of as derived from the cubic elpasolite structure: the hexacyanoferrate ions form a base lattice that is close to face-centred cubic, the tetrahedral interstices are occupied by HMT molecules, the octahedral interstices by hydrated cations. Depending on the size of the cations and the number of water molecules coordinated to the cations, distortion of the lattice occurs, and less symmetric structures result. The title compound also shows this pattern, but crystallizes in a transformed body-centred cell. The lithium hexacyanoferrate(III) compound $Li_3[Fe(CN)_6].2C_6H_{12}N_4.5H_2O$ (Pickardt, Kähler, Rautenberg & Riedel, 1984) is isostructural but possesses disordered lithium ions.

Experimental. Pale-yellow transparent crystals were obtained by diffusion of a solution of HMT in methanol into an aqueous phase containing lithium hexacyanoferrate(II). The compound was characterized by CHN analysis, C% 34·48 (calc. 35·43), H% 5·70 (5·62), N% 32·14 (32·14), and by IR spectroscopy. From Buerger precession photographs the symmetry was found to be orthorhombic, space group $Imm2$, derived from systematic absences hkl ($h+k+l = 2n+1$) and discriminated from $Immm$ *etc.* during the structure determination process. Octahedral crystal 0·20 × 0·15 × 0·15 mm; diffractometer Syntex $P2_1$, Mo $K\alpha$ radiation, graphite monochromator; cell parameters from 15 reflections

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Table 1. *Positional parameters and their estimated standard deviations*

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Fe	0·0000	0·0000	0·0000	1·77
C(1)	0·0000	0·1345 (8)	0·1455 (8)	2·40
C(2)	0·0000	0·1274 (8)	−0·1530 (8)	2·48
C(3)	0·1303 (4)	0·0000	0·0051 (11)	2·46
N(1)	0·0000	0·2243 (7)	0·2268 (8)	3·19
N(2)	0·0000	0·1997 (7)	−0·2543 (8)	3·72
N(3)	0·2104 (3)	0·0000	0·0097 (10)	3·48
N(11)	0·2862 (2)	0·6190 (3)	−0·0102 (6)	2·66
N(12)	0·1954 (4)	0·5000	0·1762 (6)	2·42
N(13)	0·1498 (4)	0·5000	−0·0879 (7)	2·65
C(11)	0·2075 (3)	0·6160 (5)	−0·1122 (6)	2·93
C(12)	0·2519 (3)	0·6174 (5)	0·1467 (5)	2·82
C(13)	0·3429 (4)	0·5000	−0·0359 (8)	2·85
C(14)	0·1179 (5)	0·5000	0·0697 (9)	2·69
Li(1)	0·0000	0·3391 (11)	0·5992 (12)	2·56
Li(2)	0·1687 (7)	0·5000	0·4126 (13)	2·78
O(1)	0·1030 (2)	0·3359 (3)	0·4501 (4)	2·43
O(2)	0·0000	0·5000	−0·2844 (11)	2·54

Table 2. *Bond distances* (Å) *and angles* (°)

Li(1)—O(1)	2·044 (8)	C(1)—N(1)	1·190 (8)
Li(1)—O(2)	1·979 (8)	C(2)—N(2)	1·189 (8)
Li(1)—N(2)	1·969 (8)	C(3)—N(3)	1·191 (7)
Li(2)—O(1)	1·993 (6)	C(11)—N(11)	1·493 (7)
Li(2)—N(3)	2·002 (6)	C(11)—N(13)	1·495 (6)
Li(2)—N(12)	2·187 (8)	C(12)—N(11)	1·516 (7)
Fe—C(1)	1·926 (8)	C(12)—N(12)	1·505 (6)
Fe—C(2)	1·922 (8)	C(13)—N(11)	1·514 (5)
Fe—C(3)	1·935 (5)	C(14)—N(12)	1·505 (9)
		C(14)—N(13)	1·511 (9)

O(2)—Li(1)—O(1)	111·6 (4)	Li(1)—N(2)—C(2)	171·8 (8)
O(2)—Li(1)—N(2)	105·0 (6)	N(13)—C(11)—N(11)	112·0 (4)
O(1)—Li(1)—N(2)	115·9 (4)	N(12)—C(12)—N(11)	111·4 (4)
O(1)—Li(2)—O(1^{i})	117·6 (4)	N(11)—C(13)—N(11^{i})	109·6 (5)
O(1)—Li(2)—N(3)	111·3 (5)	N(13)—C(14)—N(12)	111·8 (5)
O(1)—Li(2)—N(12)	104·9 (4)	C(12)—N(11)—C(11)	108·8 (3)
N(3)—Li(2)—N(12)	105·8 (5)	C(13)—N(11)—C(11)	108·8 (4)
C(1)—Fe—C(1^{i})	93·1 (5)	C(13)—N(11)—C(12)	108·9 (4)
C(2)—Fe—C(1)	89·9 (3)	C(12)—N(12)—C(12^{i})	108·3 (5)
C(2)—Fe—C(2^{i})	87·1 (5)	C(14)—N(12)—C(12)	108·2 (3)
C(3)—Fe—C(1)	89·0 (2)	C(11)—N(13)—C(11^{i})	107·4 (5)
C(3)—Fe—C(2)	91·0 (2)	C(14)—N(13)—C(11)	108·7 (4)
N(1)—C(1)—Fe	175·0 (6)	Li(2)—O(1)—Li(1)	117·7 (4)
N(2)—C(2)—Fe	175·6 (6)	Li(1)—O(2)—Li(1^{i})	115·0 (1)
N(3)—C(3)—Fe	179·4 (8)		

Symmetry code: (i) $x, -y, z$.

($2\theta \le 20°$); ω-scan mode, scan speed 0·8–29·3 °min^{-1}, depending on intensity; one octant measured up to maximum 2θ 50° ($0 \le h \le 17, 0 \le k \le 12, 0 \le l \le 10$); two standard reflections, monitored every 50 reflections, showed only random statistical fluctuations <4% during data collection. 729 unique reflections (including unobserveds) corrected for Lorentz and polarization effects, no absorption or extinction correction. All reflections were used for structure determination and refinement.

The Fe atom was fixed at the origin, light atoms then found by successive difference Fourier syntheses. Anisotropic refinement based on F. Methylene H atoms introduced at calculated positions (C—H = 1·08 Å); 129 parameters, final $R = 0{\cdot}040$, $wR = 0{\cdot}040$, $w = 1/\sigma^2(F_o)$, $S = 1{\cdot}1$, max. Δ/σ in the last cycle 0·07, largest residue peak in final difference Fourier synthesis 0·5 e Å^{-3}. Computing with *SHELX* (Sheldrick, 1976), scattering factors taken from *International Tables for X-ray Crystallography* (1974). The inverse structure refined to a somewhat higher R value of 0·043, and thus we assume the chirality to be correct.

Final atomic coordinates are given in Table 1 and bond lengths and angles in Table 2.* Fig. 1 shows a stereoview, and Fig. 2 presents a selected detail of the structure, showing the cation $[Li_4(OH_2)_5]^{4+}$ and indicating the coordination of the Li ions to the hexacyanoferrate groups and the nitrogen atoms N(12) of the HMT molecules.

The ^{57}Fe Mössbauer transmission spectrum of the title compound was recorded at room temperature with a Promeda (Elscint) spectrometer. The spectrum shows a single-line resonance with an isomer shift $\delta = 0{\cdot}079\ (2)$ mm s^{-1} relative to Fe.

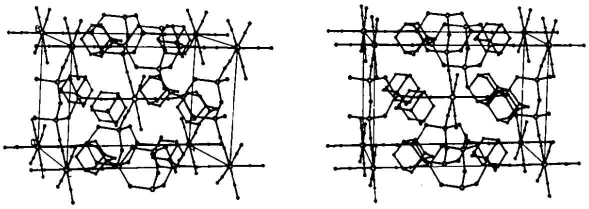

Fig. 1. Stereoscopic packing diagram of the unit-cell contents looking down the c axis. The a axis is horizontal and the b axis is vertical.

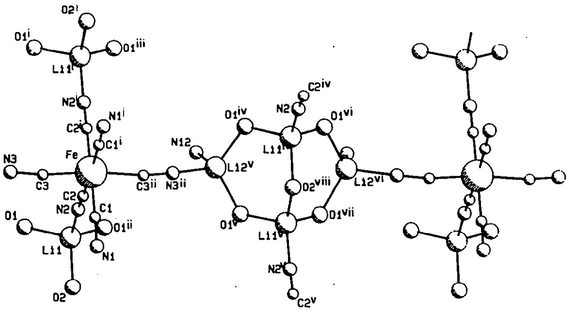

Fig. 2. Coordination of the Li ions. Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, z$; (iii) $-x, -y, z$; (iv) $\frac{1}{2}+x, y-\frac{1}{2}, z-\frac{1}{2}$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$; (vii) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51096 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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. $[NiI_2(C_{18}H_{15}P)_2]$, $M_r = 837{\cdot}09$, monoclinic, $P2_1/c$, $a = 19{\cdot}361\,(17)$, $b = 10{\cdot}220\,(5)$, $c = 17{\cdot}995\,(13)$ Å, $\beta = 112{\cdot}26\,(7)°$, $V = 3296\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}687$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}56$ mm^{-1}, $F(000) = 1640$, $T = 291$ K, $R = 0{\cdot}0780$ 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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