

51 (3)° with the plane of NiN<sub>NCS</sub>N<sub>pip</sub> [plane (1)], and an angle of 49 (3)° with the plane of four C atoms of the 2,6-Me<sub>2</sub>pip ligand [C(11)C(13)C(15)C(16)] [plane (2)]; planes (1) and (2) form an angle of 81.5 (3)°. The benzene molecule is thus trapped in the cage formed by four 2,6-Me<sub>2</sub>pip ligands of two adjacent complex molecules. The two pairs of methyl groups are directed towards benzene molecules with contacts C(17)···C(23) 3.66 (8) and C(12')···C(22) 3.64 (4) Å (Table 2), close to the van der Waals contact distance of 3.7 Å calculated as the sum of 2.0 Å for the methyl radius and 1.7 Å for the benzene half-thickness. The weak intermolecular bonding of the benzene in the crystal structure explains the rather high values of the temperature-factor coefficients of the benzene atoms (Table 1).

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## Structure of Bis(triphenylphosphine)iminium\* Bis(cyano)(phthalocyaninato)ferrate(III), [N{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>][Fe(CN)<sub>2</sub>(C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>)], at 180 K

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**Abstract.**  $M_r = 1159.0$ , triclinic,  $P\bar{1}$ ,  $a = 12.940$  (4),  $b = 12.320$  (2),  $c = 10.322$  (3) Å,  $\alpha = 65.22$  (8),  $\beta = 68.24$  (15),  $\gamma = 76.34$  (9)°,  $V = 1381.2$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.393$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 3.83$  cm<sup>-1</sup>,  $F(000) = 599$ ,  $T = 180$  K.  $R = 4.7\%$  for 3023 independent observed reflexions. The Fe<sup>III</sup>-bis(cyano)phthalocyanine anion and the bis(triphenylphosphine)iminium cation are in special positions, site symmetry  $\bar{1}$ . Thus, the P–N–P skeleton is in the very seldom observed linear configuration. The Fe–C–N arrangement is essentially linear with Fe–C = 1.974 (4) Å, angle Fe–C–N = 176.7 (3)°, in distinct contrast to the 'bent' geometry found in cyano-heme proteins.

**Introduction.** The study of metallophthalocyanines has been and continues to be of interest because of their close structural relationship to naturally occurring

oxygen carriers, their catalytic activity, and their electrical properties. Special attention is focused on the iron(III) phthalocyanines. Synthesis and spectroscopical properties of bis(cyano)(phthalocyaninato)ferrates(III), [Fe(CN)<sub>2</sub>Pc(2-)]<sup>-</sup>, isolated as the bis-(triphenylphosphine)iminium (PNP) salt, have been reported by Kalz, Homborg, Küppers, Kennedy & Murray (1984). In this paper, the structural characterization is presented.

**Experimental.** [PNP] [Fe(CN)<sub>2</sub>Pc] was crystallized by slow diffusion of HCN-containing CH<sub>2</sub>Cl<sub>2</sub> into a CH<sub>2</sub>Cl<sub>2</sub> solution of [PNP][Fe(OH)<sub>2</sub>Pc]. The bis-(hydroxo) complex was synthesized according to the procedure of Kalz & Homborg (1983). Crystal approximately isometric with edges *ca* 0.25 mm; sample temperature 180 K, Philips PW 1100 diffractometer,  $\theta$ - $2\theta$  scans, Mo  $K\alpha$  radiation; 3406 reflexions measured in  $\theta$  range 2–25°, 3023 unique;  $R_{\text{int}} = 0.035$ ; index range  $h \pm 13$ ,  $k - 12/13$ ,  $l 0/9$ ; lattice parameters by

\* Bis(triphenylphosphorane)diyl)ammonium.

least-squares fit to 63 diffractometrically determined angles, no absorption corrections; 3 standard reflexions (231, 142 and 030) monitored every 25 reflexions showed no systematic decay; variation  $\pm 7\%$ ; structure determined by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), H atoms located by difference Fourier maps; full-matrix least-squares refinement (based on  $F$ ), anisotropic temperature factors for non-H atoms, individual isotropic temperature factors for H atoms. Final  $wR = 0.034$  ( $R = 0.047$ ) for 3023 independent reflexions; all measured reflexions considered observed;  $w = 1/\sigma^2(F)$ . Isotropic extinction parameter  $g = 6.5 \times 10^{-7}$ . Scattering factors for neutral atoms from Cromer & Mann (1968). Final  $(\Delta/\sigma)_{\max} = 0.057$ . Residual electron density between  $-0.36$  and  $+0.35 e \text{ \AA}^{-3}$ ; calculations performed with *SHELX76* (Sheldrick, 1976). Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.\*

**Discussion.** Fig. 1 shows a stereoscopic view of the unit cell drawn by *ORTEP* (Johnson, 1976). One PNP unit, centred at  $[0.5, 0.5, 0.5]$ , is surrounded by eight anions; their centres are at the corners of the unit cell. The molecular packing along the  $c$  axis involves a slight overlap of peripheral phenylene groups of neighbouring phthalocyanine ligands. The distance between their mean planes,  $3.487$  (14)  $\text{\AA}$ , is within the usual range for stacked aromatic carbon compounds.

The coplanarity of the metal ion with the inner N atoms of the macrocycle strongly suggests a ( $d^5$ ) low-spin ( $S = \frac{1}{2}$ ) configuration of  $\text{Fe}^{\text{III}}$  which was also confirmed by spectroscopic investigations (Kalz *et al.*, 1984). In the series of tetraphenylporphyrin (TPP) compounds, numerous pentacoordinated (mono-ligated) Fe ions, as well as the hexacoordinated, cyanide bis-ligated Fe ion (Scheidt, Haller & Hatano, 1980), are known. It is observed that, together with the geometrical change from the mono-ligated to the bis-ligated configuration, a conversion of spin state, from intermediate- or high-spin to low-spin, takes place (Scheidt & Gouterman, 1983). The present structure is the first example of a bis-ligated  $\text{Fe}^{\text{III}}\text{Pc}$  complex. Thus, together with the known mono-ligated Pc complexes, a comparison with the TPP complexes is possible. It appears that in the Pc compounds also a change of coordination from five to six induces a change of spin state from admixed or high-spin to low-spin. This analogy further qualifies the Pc complexes as model substances for biochemically relevant redox processes.

\* Lists of structure factors, anisotropic temperature factors, H-atom coordinates and Fig. 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42255 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 2 shows one  $[\text{Fe}(\text{CN})_2\text{Pc}]^-$  unit with the interatomic distances and angles calculated with *ORFFE* (Busing, Martin & Levy, 1964). There is no remarkable deviation in intramolecular distances in comparison to other known metallophthalocyanines (Moser & Thomas, 1983). The arrangement of the axial cyano group is nearly linear  $[\text{N}-\text{C}-\text{Fe}: 176.7$  (3) $^\circ$ ]. The distances and angles around the Fe ion as reported in the preliminary note (Kalz *et al.*, 1984) require small corrections. The correct values are given in this paper.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

$U_{\text{eq}}$  is one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U_{\text{eq}}$
Fe	0	10000	10000	176 (2)
N(1)	-185 (2)	12210 (2)	6735 (3)	184 (6)
N(2)	477 (2)	10140 (2)	7924 (3)	161 (7)
N(3)	1426 (2)	8146 (2)	8151 (3)	180 (6)
N(4)	642 (2)	8338 (2)	10580 (3)	169 (6)
C(1)	340 (2)	11149 (3)	6723 (4)	186 (11)
C(2)	867 (2)	10907 (3)	5347 (4)	191 (9)
C(3)	981 (2)	11612 (3)	3839 (4)	241 (8)
C(4)	1527 (3)	11087 (3)	2809 (4)	277 (8)
C(5)	1964 (3)	9886 (3)	3208 (4)	284 (9)
C(6)	1884 (2)	9198 (3)	4686 (4)	249 (7)
C(7)	1317 (2)	9716 (3)	5760 (4)	194 (8)
C(8)	1077 (2)	9250 (3)	7383 (4)	187 (9)
C(9)	1228 (2)	7750 (3)	9610 (4)	188 (8)
C(10)	1632 (2)	6552 (3)	10449 (4)	191 (8)
C(11)	2256 (2)	5598 (3)	10033 (4)	247 (8)
C(12)	2513 (3)	4561 (3)	11112 (4)	285 (9)
C(13)	2138 (3)	4444 (3)	12626 (4)	302 (8)
C(14)	1511 (3)	5381 (3)	13065 (4)	263 (7)
C(15)	1268 (2)	6432 (3)	11953 (4)	192 (9)
C(16)	643 (2)	7580 (3)	12008 (3)	187 (8)
C(CN)	1474 (3)	10477 (2)	9601 (3)	175 (7)
N(CN)	2355 (2)	10709 (2)	9349 (3)	295 (5)
P	4361 (1)	3879 (1)	6116 (1)	214 (2)
N(P)	5000	5000	5000	323 (8)
C(21)	4939 (2)	3081 (3)	7627 (4)	241 (7)
C(22)	5171 (3)	1840 (3)	8154 (4)	331 (8)
C(23)	5711 (3)	1289 (3)	9241 (4)	377 (7)
C(24)	6027 (3)	1960 (3)	9772 (4)	375 (8)
C(25)	5760 (3)	3178 (4)	9310 (5)	445 (10)
C(26)	5237 (3)	3751 (3)	8215 (4)	365 (8)
C(31)	2909 (2)	4332 (3)	6868 (4)	204 (9)
C(32)	2251 (3)	3621 (3)	8265 (4)	243 (8)
C(33)	1135 (3)	3990 (3)	8793 (4)	280 (7)
C(34)	678 (2)	5053 (3)	7951 (4)	274 (8)
C(35)	1324 (3)	5746 (3)	6576 (4)	330 (8)
C(36)	2440 (3)	5402 (3)	6012 (4)	270 (7)
C(41)	4462 (2)	2874 (3)	5210 (4)	208 (8)
C(42)	5463 (3)	2723 (3)	4145 (4)	304 (7)
C(43)	5590 (3)	1963 (3)	3424 (4)	362 (8)
C(44)	4698 (3)	1354 (3)	3756 (5)	365 (9)
C(45)	3699 (3)	1483 (3)	4821 (4)	327 (6)
C(46)	3579 (3)	2239 (3)	5566 (4)	275 (7)

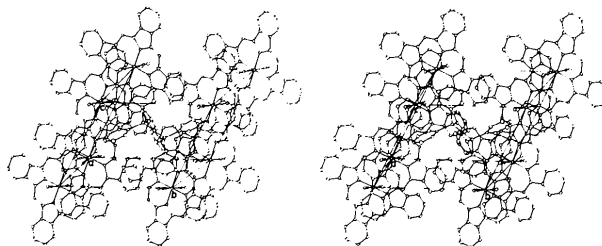


Fig. 1. Stereoscopic view of the unit cell along  $a^*$ . H atoms are omitted.

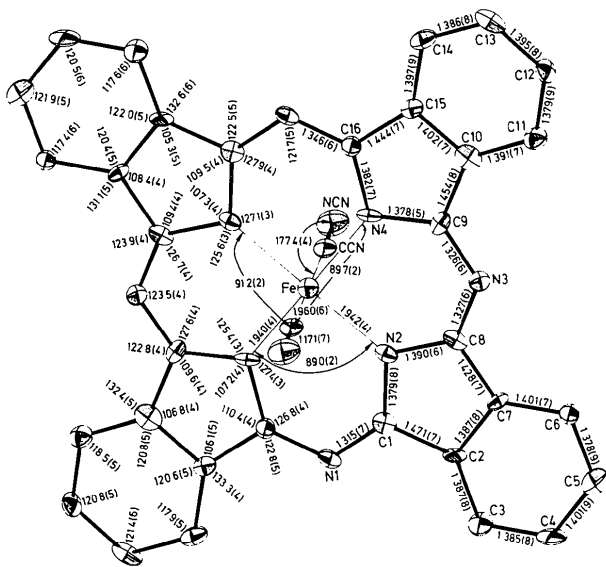


Fig. 2. ORTEP plot of the  $[Fe(CN)_2Pc]^-$  anion with bond lengths (Å) (right part of the centrosymmetrical anion) and angles ( $^\circ$ ) (left part). Thermal ellipsoids are at the 50% probability level.

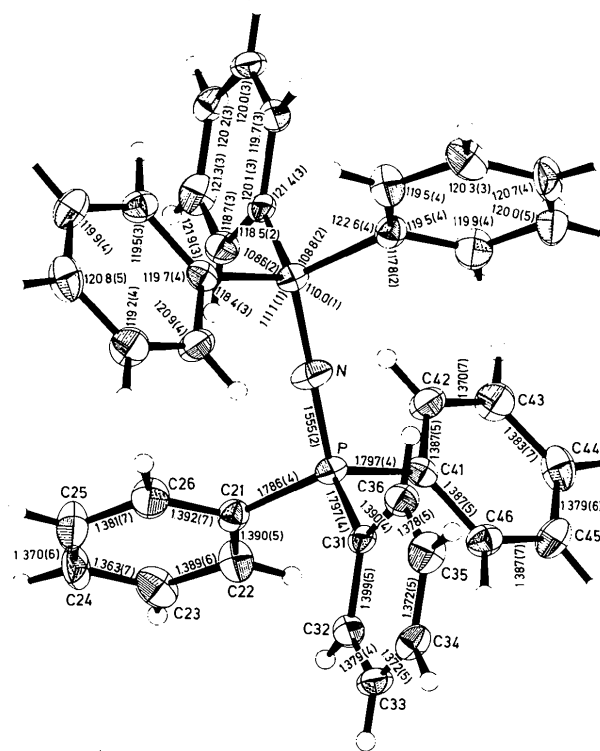


Fig. 3. ORTEP plot of the PNP cation with bond lengths (Å) (lower part of the centrosymmetrical group) and angles ( $^\circ$ ) (upper part). Probability level 50%. A common, arbitrary temperature factor was chosen for the H atoms. Two angles which could not be inserted in a clear manner are:  $C(21)-P-C(41) = 108.2(2)$  and  $C(31)-P-N = 110.1(2)^\circ$ .

Since the CN stretching vibration could not be observed, the possibility of ambident N-bound cyanide, as reported in Prussian blue analogues (Shriver, 1966), was taken into consideration. After interchanging the C and N positions in the CN group, the refinement converged at a final  $wR = 0.037$ , which is significantly higher than  $wR = 0.034$  obtained with the 'usual' CN order.

The PNP cation represented in Fig. 3 has  $\bar{1}$  site symmetry. The P–N–P angle is, therefore,  $180^\circ$ . This linear configuration is observed only in a few examples. The Cambridge Structural Database (1984) lists 97 structures containing PNP cations; only four show linear or quasilinear configurations. The other 93 exhibit the bent configuration with a mean P–N–P angle of  $142.6^\circ$  (standard deviation  $6.3^\circ$ ). Of the four 'linear' PNP cations, one has a P–N–P angle of  $175.6^\circ$  (Longoni, Manassero & Sansoni, 1979) and three have a  $180^\circ$  angle. In two of the latter three (Kirtley, Chanton, Love, Tipton, Sorrell & Bau, 1980; Usón, Laguna, Laguna, Jones & Sheldrick, 1981), the cation has  $\bar{1}$  symmetry and, in the third case, Wilson & Bau (1974) and Calderazzo, Pampaloni & Pelizzi (1982) found  $\bar{3}$  symmetry in two isostructural compounds. In the structure discussed here the PNP cation also has approximate  $\bar{3}$  symmetry. A visual impression of the quasi threefold axis is given by Fig. 4.\* This is further supported by the similarity of the N–P–C angles [ $110.0(1)$ ,  $110.1(1)$ ,  $111.1(1)^\circ$ ], the C–P–C angles [ $108.2(2)$ ,  $108.6(2)$ ,  $108.8(2)^\circ$ ], and the dihedral angles between the mean planes through the phenyl groups [ $87.2(8)$ ,  $85.7(9)$ ,  $78.4(4)^\circ$ ]; the scatter of these dihedral angles is frequently used as a measure of the deviation from threefold symmetry (Handy, Ruff & Dahl, 1970). The N–P distances are found to be shorter in the linear PNP cations than in the bent ones.

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\* See previous footnote.

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## Octahedral Nickel Dioxime Iodides: Bis(oxamide oxime)(oxamide oximium)nickel(II) Triiodide Hydrate and *cis*-Diiodobis(oxamide oxime)nickel(II)

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**Abstract.** Room temperature,  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ .  $[\text{Ni}(\text{C}_2\text{H}_7\text{N}_4\text{O}_2)(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_2]\text{I}_3 \cdot \text{H}_2\text{O}$ :  $M_r = 812.73$ , trigonal,  $R3c$ ,  $a = 16.218(3)$ ,  $c = 14.562(3) \text{ \AA}$ ,  $V = 3317 \text{ \AA}^3$ ,  $Z = 6$ ,  $D_x = 2.44 \text{ g cm}^{-3}$ ,  $\mu = 48 \text{ cm}^{-1}$ ,  $F(000) = 2304$ , final  $R = 0.045$  for 860 observed independent reflections. In the tripositive complex cation  $\text{Ni}^{\text{II}}$ , site symmetry 32, is octahedrally coordinated by three oxamide oxime chelate ligands [Ni–N, 2.055(5)  $\text{ \AA}$ ], one of which is protonated to a monocationic species.  $[\text{NiI}_2(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)_2]$ :  $M_r = 548.71$ , monoclinic,  $P2_1/a$ ,  $a = 13.444(2)$ ,  $b = 7.830(2)$ ,  $c = 15.222(3) \text{ \AA}$ ,  $\beta = 115.42(1)^\circ$ ,  $V = 1447.2 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 2.52 \text{ g cm}^{-3}$ ,  $\mu = 55.9 \text{ cm}^{-1}$ ,  $F(000) = 1032$ , final  $R = 0.032$  for 3037 observed independent reflections. The crystals consist of neutral octahedral *cis*-diiodobis(oxamide oxime)nickel(II) complexes, Ni–N, 2.034(4)–2.061(4)  $\text{ \AA}$ , Ni–I, 2.806(1), 2.851(1)  $\text{ \AA}$ .

**Introduction.** Iodine oxidation of stacked square-planar metal complexes, especially complexes of the Ni triad with dioximato or tetraazamacrocyclic ligands, may lead to solids with enhanced electrical conductivity and with interesting structural properties (Endres, Keller, M\u00e9gnamisi-B\u00e9lomb\u00e9, Moroni, Pritzkow, Weiss & Com\u00e8s, 1976; Cowie, Gleizes, Grynkewich, Kalina,

McClure, Scaringe, Teitelbaum, Ruby, Ibers, Kannewurf & Marks, 1979; Hunziker, Hilti & Rihs, 1981; Hoffman & Ibers, 1983). Having synthesized new molecular conductors with oxamide oxime [ $\text{‘oaoH}_2\text{’}$ ,  $\text{HON}=\text{C}(\text{NH}_2)-\text{C}(\text{NH}_2)=\text{NOH}$ ] metal complex cations and organic radical anions (Endres, 1982, 1984a; Endres, Bongart, N\u00f6the, Hennig, Schweitzer, Sch\u00e4fer, Helberg & Flandrois, 1985), we also tried to prepare partially oxidized oxamide oxime metal complexes by iodine oxidation. As in the case of Pt, where the unoxidized salt  $[\text{Pt}(\text{oaoH})(\text{oaoH}_2)]\text{I} \cdot 2\text{H}_2\text{O}$  was obtained (Endres, 1985), no oxidation took place with the Ni complex. The two title species were formed instead.

**Experimental.** The two compounds were obtained together in varying ratios. Mainly  $[\text{Ni}(\text{oaoH}_3)(\text{oaoH}_2)_2]\text{I}_3 \cdot \text{H}_2\text{O}$  obtained on dissolving  $[\text{Ni}(\text{oaoH}_2)_3]\text{Cl}_2$  (Tschugaeff & Surenjanz, 1907; Endres & Jannack, 1980) in  $\text{H}_2\text{O}$ , adding NaI and  $\text{I}_2$  and stirring at room temperature. Filtered, green filtrate allowed to evaporate, turning blue after some days. Dark-violet rhombohedrally shaped crystals of the triiodide formed together with small amount of green {most likely  $[\text{NiI}_2(\text{oaoH}_2)_2]$ } and blue (starting complex) material. Triiodide also forms on dissolving  $[\text{Ni}(\text{oaoH})_2]$  in