Inorganica Chimica Acta, 204 (1993) 181–187

Synthesis and characterization of $[N(PPh_3)_2]^+$ cyanometallates. Crystal structure of $[N(PPh_3)_2]_3[Fe(CN)_6] \cdot 2H_2O$

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(Received July 30, 1992)

Abstract

The complex salts $[N(PPh_3)_2]_n[M(CN)_6]$ (M = Fe, $n=3$ or 4; M = Ru, $n=4$; M = Co, $n=3$) and $[N(PPh_3)_2]_2[Fe(CN)_5(NO)]$ have been prepared by metathetical reactions between $[N(PPh_3)_2]Cl$ and the corresponding alkaline cyanometallates. The iron(II) and ruthenium(II) hexacyano complexes are rather unstable in the air, the former being completely oxidized in a short time even in the solid state. All compounds have been characterized by spectroscopic techniques. The crystal structure of $[N(PPh_3)_2]_3[Fe(CN)_6] \cdot 2H_2O$ has been determined by X-ray diffraction methods.

Introduction

The bridging properties of the cyanide group and its outstanding capability to stabilize mixed valence systems are well known in inorganic chemistry: the prussian blue and its related compounds are emblematic examples of these features [1]. Owing to their structural and electronic characteristics some cyanometallate salts exhibit interesting properties, e.g. molecular sieve properties [2] and photochemical activity [3]. Furthermore the cyanide bridge has been recently used to 'build-up' molecular systems where a photosensibilisator is covalently bonded to a fragment that can behave as a donor or acceptor of energy [4].

During recent years, the properties of the cyanide ligand have found new applications in organometallic chemistry, mainly directed to the production of molecules with unusual geometries, such as rows of atoms or cage structures, where the CN group is bridging different metal centers [5]. A building strategy for obtaining this kind of molecule is to react the suitable cyanometallates with electrophilic organometallic fragments.

The reactivity of cyanometallates towards molecules containing electrophilic centers is high and, in some cases, the bridging process is in fact a polymerization reaction. Organotin compounds such as R_3SnX (X = halogen, R = alkyl or aryl), react with $K_n[M(CN)_6]$ (M = Fe, Ru or Co) to give polymeric products of formula $[(R_3Sn)_nM(CN)_6]_\infty$, which can act as host systems as well as efficient ion exchangers and receptors for organic and organometallic cations [6].

Sometimes, the low solubility of cyanometallates in organic solvents, due to the nature of the countercation (normally an alkaline metal), is a problem in performing these reactions. Therefore, in order to improve the solubility of these salts in organic media, we have replaced the alkaline cation with the bis(triphenylphosphino)iminium ion [7], $[N(PPh_3)_2]^+$, which is widely used in organometallic chemistry to stabilize large anionic clusters. Another advantage of using this cation is the enhancement of the nucleophilic power of the anion, which is important for performing bridging reactions. Substitution of the potassium ion with $[N(PPh_3)_2]^+$ allowed the reactivity of these cyanometallates to be changed; e.g. by reacting $[N(PPh_3)_2]_3[Fe(CN)_6]$ with Ph_3SnCl in Me_2SO, the unusual trinuclear anion $[(Ph_3SnCl)_2(\mu\text{-}CN)_2Fe(CN)_2(Me_2SO)_2]^{2-}$ was obtained, in place of the polymeric materials given by the corresponding potassium salt [5a, 6h].

This paper deals with the synthesis and characterization of the following $[N(PPh_3)_2]^+$ cyanometallates: hexacyanoferrate(III) (**1**), hexacyanoferrate(II) (**2**), hexacyanoruthenate(II) (**3**), hexacyanocobaltate(III)

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0020-1693/93/$6.00

(4), pentacyanonitrosylferrate(III) (5), starting from commercial potassium or sodium salts. These complex salts have been prepared with the purpose of obtaining versatile starting materials for the kind of reactions described above. The preparations of $[N(PPh_3)_2]_4[Mo(CN)_8]$ and $[N(PPh_3)_2]_2[Co(CN)_4]$ have been previously described [8].

Results and discussion

The $[N(PPh_3)_2]^+$ cyanometallates have been prepared in high yield (more than 95%) by precipitation from a warm aqueous solution of $[N(PPh_3)_2]Cl$ added to a solution of the corresponding alkaline salts, using a small excess of cyanometallate. They are very soluble in most polar aprotic solvents: acetonitrile, acetone, dimethyl sulfoxide, alcohols and chlorinated solvents, but insoluble in ethers and aliphatic or aromatic hydrocarbons; this is, in general, the behaviour of all inorganic salts of $[N(PPh_3)_2]^+$ [7].

These products are air stable with the exception of **2** and **3**. When exposed to the air, compound **2** is completely oxidized in about one week in the solid state, and very quickly in acetone solution (IR monitoring). Its instability is probably due to the absence of strong cation–anion interactions (as in the alkaline salts), so that the hexacyano anion, that bears four negative charges, becomes more reactive and easy to oxidize. The ruthenium compound **3** is fairly unstable and oxidizes very slowly when exposed to the air even in acetone solution. It has been reported recently that $[NBu_4]_4[Ru(CN)_6]$, in dimethylformamide, oxidizes by a fast process [9].

The characterization of these products has been made by IR spectroscopy and, in the case of **1** and **5**, by Mössbauer spectroscopy; furthermore the electrochemical properties of the $[N(PPh_3)_2]_4[Fe(CN)_6]$/ $[N(PPh_3)_2]_3[Fe(CN)_6]$ system have been studied by cyclic voltammetry. The ^{57}Co NMR spectrum of $[N(PPh_3)_2]_3[Co(CN)_6]$ in $CDCl_3$ solution shows a single peak at 279 ppm, whose small linewidth (20 Hz) is typical of a high-symmetry species.

Infrared spectra

The main IR absorption bands, compared with those of the starting salts, are reported in Table 1. The most important feature is the lowering of the CN stretching frequencies in consequence of the cation substitution; the mean lowering of the stretching frequency is about 20 cm^{-1}. This is probably due to the lowered interactions between the cation and the nitrogen atom of the cyanogroups; in fact, the stretching frequency of the CN group is enhanced by forming a metal–metal bridge, as the CN group uses antibonding orbitals for the σ-donation and the π-backdonation (that should weaken the bond) is lowered by the negative charge [5f]. In the case of alkaline cyanometallates there is not really a bridge formation, but the electrostatic interaction causes the frequency enhancement. This kind of interaction, even if present, is certainly weaker when the countercation is $[N(PPh_3)_2]^+$. The enhancement of the negative charge density accounts also for the nitrosyl stretching shift (see Table 1) in **5**.

TABLE 1. Main νCN IR bands (cm^{-1}) for **1–5** and their alkaline precursors (Nujol mulls)

Compound	νCN (cm^{-1})	νNO (cm^{-1})
$K_3[Fe(CN)_6]$	2120 2116	
$[N(PPh_3)_2]_3[Fe(CN)_6]$	2104 2099 2093	
$K_4[Fe(CN)_6]$	2049 2042	
$[N(PPh_3)_2]_4[Fe(CN)_6]$	2041 2017	
$K_4[Ru(CN)_6]$	2110 2084 2053 2037	
$[N(PPh_3)_2]_4[Ru(CN)_6]$	2024	
$K_3[Co(CN)_6]$	2132 2128	
$[N(PPh_3)_2]_3[Co(CN)_6]$	2113 2106 2104	
$Na_2[Fe(CN)_5NO]$	2174 2163 2158 2144	1939
$[N(PPh_3)_2]_2[Fe(CN)_5NO]$	2136 2130	1869

The Nujol mull technique must be used instead of the KBr disc technique in order to avoid cation exchange during sample preparation. The spectra of samples registered as KBr discs gave the appearance of different bands probably due to the presence of mixed cation species.

Description of the crystal structure of $[N(PPh_3)_2]_3[Fe(CN)_6]\cdot 2H_2O$ ($1\cdot 2H_2O$)

The crystal structure of $\mathbf{1}\cdot 2H_2O$ consists of $[Fe(CN)_6]^{3-}$ anions, $[N(PPh_3)_2]^+$ cations and water molecules. The Fe atom lies on a two-fold axis so that the $[Fe(CN)_6]^{3-}$ anion has an imposed C_2 symmetry. Two crystallographically independent, even if structurally very similar, $[N(PPh_3)_2]^+$ cations are present, the former occupies a general position, whereas the nitrogen atom of the latter lies on a two-fold axis, so that the cation has an imposed C_2 symmetry. Because of the different multiplicity these two types of cations are in a 2:1 ratio. The structure of the anion is shown in Fig. 1. The most significant bond distances and angles in the cations and in the anion are given in Table 2.

Several structural data on the $[Fe(CN)_6]^{3-}$ anion in salts with different cations have been reported up to now [10–14]. The most significant ones are compared with those found in $\mathbf{1}\cdot 2H_2O$ in Table 3. In spite of the presence of different cations only small differences

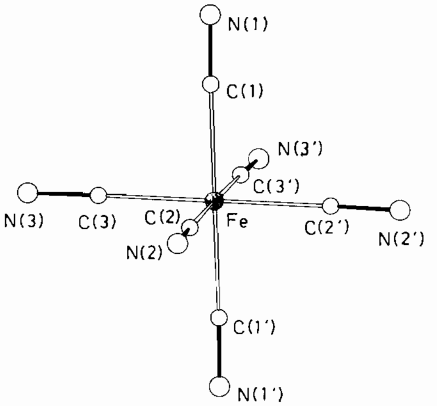

Fig. 1. View of the structure of the $[Fe(CN)_6]^{3-}$ anion of **1** with the atomic numbering scheme.

TABLE 2. Relevant bond distances (Å) and angles (°) in $[N(PPh_3)_2]_3[Fe(CN)_6]\cdot 2H_2O$[a]

Fe–C(1)	1.952(8)	C(1)–N(1)	1.151(10)
Fe–C(2)	1.935(7)	C(2)–N(2)	1.165(10)
Fe–C(3)	1.935(7)	C(3)–N(3)	1.169(10)
N(4)–P(1)	1.585(7)	P(2)–C(22)	1.794(9)
N(4)–P(2)	1.569(7)	P(2)–C(28)	1.804(10)
N(5)–P(3)	1.582(3)	P(2)–C(34)	1.803(9)
P(1)–C(4)	1.798(8)	P(3)–C(40)	1.806(7)
P(1)–C(10)	1.801(10)	P(3)–C(46)	1.798(7)
P(1)–C(16)	1.788(9)	P(3)–C(52)	1.793(6)
C(1)–Fe–C(2)	90.5(3)	Fe–C(1)–N(1)	179.4(7)
C(1)–Fe–C(3)	91.4(3)	Fe–C(2)–N(2)	177.4(6)
C(2)–Fe–C(3)	92.6(3)	Fe–C(3)–N(3)	178.4(7)
P(1)–N(4)–P(2)	140.7(4)	P(3)–N(5)–P(3′)	141.9(2)

[a] The primed atoms are related to the unprimed ones by the transformation :$1-x, y, \frac{1}{2}-z$.

in these parameters are observed, moreover the generally limited accuracy of them does not allow any certain correlation.

A probable hydrogen bond involves the water molecule and the N(3) atom of a cyanide ligand. Even if from the structural analysis it was not possible to localize the hydrogen atoms of the water molecule, the rather short N(3)...O distance, 2.800(15) Å, should be indicative of the presence of a hydrogen bond, involving the water molecule and the N(3) atom of a cyanide ligand.

Mössbauer spectra

Mössbauer spectra of **1** and **5** have been recorded and the isomer shifts (*IS*), quadrupolar splittings (*QS*) and linewidths (*LW*) are reported in Table 4 and compared with those of the starting alkaline cyano complexes [15, 16]. Both *IS* and *QS* change with cation substitution. The influence of the cation on *IS* depends on its polarizing power; in fact the polarization of the cyanide groups results in an enhanced delocalization of the non-bonding 3d electrons and hence in decreasing *IS* [15]. $[N(PPh_3)_2]^+$ is a very weakly polarizing cation and its effect is observed in **1** ($\Delta IS=0.032$ mm/s); in the case of **5** there is a little variation ($\Delta IS=0.004$ mm/s) probably because the very strong NO^+ retrodonating effect is predominant. The *QS* values of the $[N(PPh_3)_2]^+$ salts **1** and **5** are higher than those of alkaline cyanoferrates; the variation of *QS* values owing to cation substitution is about 0.2 mm/s for both compounds.

Cyclic voltammetry studies

The electrochemical properties of the $[N(PPh_3)_2]_4[Fe(CN)_6]/[N(PPh_3)_2]_3[Fe(CN)_6]$ system have been studied by means of cyclic voltammetry. Measurements have been carried out in acetonitrile, using $[NBu_4][PF_6]$ 0.05 M as supporting electrolyte, and Hg, glassy carbon (GC), Pt and Au, as working electrodes. Preliminary studies on $[N(PPh_3)_2]Cl$ showed that the $[N(PPh_3)_2]^+$ cation behaves as non-electroactive and that, on Pt and Au electrodes, it prevents, because of adsorption phenomena, any electrochemical response. In fact only on GC and Hg electrodes does the whole system $[N(PPh_3)_2]_4[Fe(CN)_6]/[N(PPh_3)_2]_3[Fe(CN)_6]$ show a quasi-reversible behaviour, which must be due to the electroactive $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ system. E_{p_a} and E_{p_c} together with i_{p_a} and i_{p_c} are listed for both Hg and GC electrodes, in Table 5.

As the ΔE_p values at low potential scan rate agree with that of ferrocene (90 mV on GC and Hg), one electron should be involved in the electrochemical reaction. The increasing values of ΔE_p versus scan rate seem to point out that a quasi-reversible process is at hand. The process is more reversible on Hg than on GC, as the quantity $K_s/(D_o/D_r)^{\alpha}/2$ (K_s is the standard rate constant, D_o and D_r the diffusion constants of $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$, respectively, and α the charge transfer coefficient) resulting from the voltammograms at different potential sweep rates on Hg is about twice that on GC [17].

As it is known that the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ system undergoes an outer-sphere electron transfer, and therefore its rate constant is independent of the electrode material [18], this difference must be explained by the adsorption of the $[N(PPh_3)_2]^+$ cation on the electrode [19].

The E_p value of $[N(PPh_3)_2]_3[Fe(CN)_6]$ versus ferrocene of -1400 mV, is in agreement with the values found in the literature for hexacyanoferrates of ammonium salts in acetonitrile [20]. This suggests that the $[N(PPh_3)_2]^+$ cation does not affect the thermodynamics of the electrochemical reaction. On the other hand no further studies at different concentrations of $[N(PPh_3)_2]^+$ were possible, owing to the irreproducible voltammograms obtained after addition of $[N(PPh_3)_2]Cl$

TABLE 3. Comparison of bond distances and bond angles in some cyanoferrates(III)

	Fe–C distances (Å)	C–N distances (Å)	Fe–C–N angles (°)	C–Fe–C angles (°)[a]	Shortest cation–NC contacts (Å)
$[(Ph_3P)_2N]_3[Fe(CN)_6]$	1.952(8) 1.935(7) 1.935(7)	1.151(10) 1.165(10) 1.169(10)	179.4(7) 177.4(6) 178.4(7)	90.5(3) 92.6(3)	3.230(11)[b] 3.311(12) 3.430(17)
$K_3[Fe(CN)_6]$ [10]	1.927(14) 1.952(16) 1.971(19)	1.131(22) 1.131(23) 1.167(26)	171.4(15) 176.6(18) 179.1(16)	88.4(7) 91.6(7)	2.827(17) 2.809(18) 2.860(18)
$Cs_2Li[Fe(CN)_6]$ [11]	1.926(3)	1.148(5)	180	90	Cs–N 3.726(1) Li–N 2.212(3)
$Cs_2Na[Fe(CN)_6]$ [11]	1.917(10) 1.939(10) 1.924(11)	1.155(14) 1.133(15) 1.152(15)	178.8(10) 178.4(10) 177.7(11)	89.5(4) 90.5(4)	Cs–N 3.307(11) 3.365(11) Na–N 2.487(10) 2.462(10)
$Cs_2K[Fe(CN)_6]$ [11]	1.930(11) 1.924(11) 1.921(11)	1.158(16) 1.159(17) 1.146(16)	178.5(11) 179.2(11) 177.4(11)	89.2(5) 90.8(5)	Cs–N 3.215(13) 3.237(13) K–N 2.789(11) 2.797(11)
$[(CH_3)_4N]_2Cs[Fe(CN)_6]$ [12]	1.934(6)	1.157(7)	178.3(9)	89.8(5)	Cs–N 3.262(6)
$[(CH_3)_4N]_2Na[Fe(CN)_6]$ [13]	1.946(2) 1.934(2) 1.952(3) 1.926(3)	1.141(3) 1.139(3) 1.128(4) 1.147(5)	177.2(2) 178.4(2) 176.9(3) 178.7(4)	87.2(1) 94.4(1)	Na–N 2.380(3) 2.413(3)
$[(CH_3)_4N]_3[Fe(CN)_6]$ [14]	1.935(5) 1.959(5) 1.946(8) 1.965(8) 1.955(8) 1.959(8)	1.156(7) 1.136(7) 1.141(11) 1.134(11) 1.131(11) 1.140(10)	178.8(9) 178.3(7) 179.3(7) 178.4(6) 178.1(8) 179.2(7)	87.9(3) 91.2(3)	

[a] Minimum and maximum. [b] C(Ph)·····N≡C–.

TABLE 4. Mössbauer parameters for **1** and **5** and their alkaline precursors

Compound	Isomer shift[a] (mm/s)	Quadrupolar splitting (mm/s)	Linewidth (mm/s)
$K_3[Fe(CN)_6]$	−0.123	0.280	0.26
$[N(PPh_3)_2]C_3[Fe(CN)_6]$	−0.091	0.499	0.15
$Na_2[Fe(CN)_5NO]$	−0.259	1.712	0.26
$[N(PPh_3)_2]_2[Fe(CN)_5NO]$	−0.255	1.935	0.18

[a] Referred to metallic iron.

to the $[N(PPh_3)_2]_3[Fe(CN)_6]$ solution, probably due to absorption phenomena. The shape of the plot of i_{p_a}/i_{p_c} versus the logarithm of potential sweep rate, agrees with a C_rE_r mechanism [21] (i_{p_a} and i_{p_a}/i_{p_c} were determined according to the method reported in ref. 22). Owing to the simplicity of the system, the most probable reversible chemical reaction preceding the electrochemical one should be the dissociation of the ionic couple $[NBu_4]^+[Fe(CN)_6]^{3-}$.

Experimental

Solvents were purified using published procedures [23]. All alkaline cyanometallates and $[N(PPh_3)_2]Cl$ were commercially available (Aldrich and Alfa Ventron) and were not further purified.

TABLE 5. Cyclic voltammetry parameters for the $[N(PPh_3)_2]_4[Fe(CN)_6]/[N(PPh_3)_2]_3[Fe(CN)_6]$ system at Hg and GC electrodes. Ferrocene is the reference system for the E_p values

	Scan rate (mV/s)	E_{pa} (mV)	E_{pc} (mV)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}
Hg	50	−880	−980	15.0	15.9	1.060
	100	−880	−980	21.8	23.5	1.078
	200	−880	−990	29.3	32.8	1.119
	400	−870	−1000	38.2	43.6	1.141
	800	−850	−1020	48.0	55.4	1.154
	2000	−830	−1050	74.6	87.4	1.171
	4000	−805	−1180	103.0	121.7	1.181
GC	50	−870	−970	15.7	15.8	1.006
	100	−860	−980	20.8	22.2	1.067
	200	−850	−990	27.0	30.4	1.146
	400	−840	−1010	34.3	39.3	1.168
	800	−820	−1050	44.5	52.0	1.201
	2000	−780	−1110	67.0	80.5	1.201
	4000	−740	−1170	91.8	111.7	1.217

Elemental analyses for C, H and N were performed on a Carlo Erba Instrumentation EA1108 automatic analyzer. IR spectra (4000–400 cm^{-1}) were recorded on a Nicolet 5PC Fourier Transformer spectrophotometer. The electrochemical measurements were performed on a three-electrode system Metrohm Polarecord E 506 (using an Ag/AgCl/KCl 3 M/$[NBu_4][PF_6]$ 0.05 M electrode as reference and a Pt electrode as counter electrode) equipped with a voltage scanner Metrohm VA E612; an analogical X-Y Linseis recorder was employed for scan rates up to 200 mV/s, while for higher rates, the analogical output of the polarograph was converted to digital by an L8200 Linseis A/D converter and collected with a PC. The solutions were prepared by dissolving $[NBu_4][PF_6]$ in acetonitrile, freshly distilled under nitrogen, up to a concentration of 0.05 M. The ^{57}Fe absorption Mössbauer measurements were performed by using a conventional spectrometer working at constant acceleration, equipped with a 20-mCi ^{57}Co source in a rhodium matrix; experiments were carried out at room temperature. ^{57}Co NMR spectra were recorded on a Bruker CXP 200 spectrometer at 47.4 MHz, using aqueous $K_3[Co(CN)_6]$ as external reference.

Preparation of $[N(PPh_3)_2]_3[Fe(CN)_6]$ (1)

A warm (40–50 °C) aqueous solution of $K_3[Fe(CN)_6]$ (0.3 g in 20 ml of water) was added dropwise to a warm stirred solution of $[N(PPh_3)_2]Cl$ (1 g in 60 ml of water). A powdery, yellow precipitate was obtained; after 10 min the solid was filtered, washed with warm water and then dried at 80 °C; yield more than 95%. The same reaction could be carried out, without heating, dissolving the $[N(PPh_3)_2]Cl$ in water with a few drops of ethanol (5–10 drops in 50 ml of water); yield more than 95%. *Anal.* Found: C, 75.1; H, 5.1; N, 6.7. Calc.: C, 74.916; H, 4.963; N, 6.897%. IR: 2126vw, 2104s, 2099s, 2093s. Mössbauer: *IS* −0.091, *QS* 0.499, *LW* 0.15.

Preparation of $[N(PPh_3)_2]_4[Fe(CN)_6]$ (2)

The reaction was carried out under inert atmosphere. $[N(PPh_3)_2]Cl$ (1 g), $K_4[Fe(CN)_6]\cdot 2H_2O$ (0.35 g) were dissolved separately in oxygen-free warm water. The hexacyanoferrate solution was added dropwise to the stirred $[N(PPh_3)_2]Cl$ solution and a pale yellow solid was obtained. It is very important to maintain the solution moderately hot to avoid the formation of an oily suspension. The product was washed with warm water and dried *in vacuo*. The dry product is brown and absorbs moisture very rapidly, returning to yellow. $[N(PPh_3)_2]_4[Fe(CN)_6]$ is not air stable and must be stored under nitrogen atmosphere. In acetone oxidation occurs in a few minutes and the Fe(III) derivative is produced. Its instability prevented the acquisition of reliable elemental analyses and Mössbauer data. IR: 2041m, 2024sh, 2017vs, 2009s.

Preparation of $[N(PPh_3)_2]_4[Ru(CN)_6]$ (3)

The reaction conditions are the same as those used for **2**, starting from $K_4[Ru(CN)_6]\cdot 3H_2O$. IR: 2117vw, 2098vw, 2024vs.

Preparation of $[N(PPh_3)_2]_3[Co(CN)_6]$ (4)

The procedure is the same as that used for the preparation of $[N(PPh_3)_2]_3[Fe(CN)_6]$. The product obtained is a white solid; yield more than 95%. *Anal.* Found: C, 75.2; H, 5.2; N, 6.8. Calc.: C, 74.790; H, 4.955; N, 6.885%. IR: 2113m, 2106s, 2104s. ^{57}Co NMR: δ 279 ppm, singlet.

Preparation of $[N(PPh_3)_2]_2[Fe(CN)_5NO]$ (5)

The procedure is the same as that used for the preparation of $[N(PPh_3)_2]_3[Fe(CN)_6]$. The product obtained is a white solid; yield more than 95%. *Anal.* Found: C, 71.7; H, 4.7; N, 8.6. Calc: C, 71.521; H, 4.677; N, 8.665%. IR: 2139msh, 2136s, 2130m, 1869vs (νNO). Mössbauer: *IS* −0.255, *QS* 1.935, *LW* 0.18.

Crystallography

Crystal data

$C_{114}H_{90}FeN_9P_6\cdot 2H_2O$, **1**$\cdot 2H_2O$, $M = 1365.41$, orthorhombic, space group *Pbcn*, $a = 23.900(7)$, $b = 20.792(5)$, $c = 19.552(5)$ Å, $U = 9716(4)$ Å^3, $Z = 4$, $D_c = 1.274$ g cm^{-3}, $F(000) = 3892$, μ(Cu Kα) = 26.27 cm^{-1}.

Data collection, structure determination and refinement of $[N(PPh_3)_2]_3[Fe(CN)_6]\cdot 2H_2O$

A crystal of approximate dimensions 0.20 × 0.22 × 0.30 mm (obtained by slow evaporation of an acetone solution) was used for the analysis. Unit cell parameters

TABLE 6. Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of $[N(PPh_3)_2]_3[Fe(CN)_6] \cdot 2H_2O$

Atom	*x/a*	*y/b*	*z/c*
Fe	0	2287(1)	2500
P(1)	2171(1)	629(1)	131(1)
P(2)	2216(1)	−402(1)	1182(1)
P(3)	5345(1)	2080(1)	3140(1)
O	880(6)	4084(6)	578(7)
N(1)	1270(3)	2276(3)	2827(4)
N(2)	162(3)	1187(3)	1449(3)
N(3)	167(3)	3350(3)	1404(4)
N(4)	2216(3)	287(3)	854(3)
N(5)	5000	2325(4)	2500
C(1)	799(3)	2282(3)	2709(4)
C(2)	107(3)	1611(3)	1833(4)
C(3)	102(3)	2957(3)	1824(4)
C(4)	1745(3)	1338(4)	213(4)
C(5)	1648(4)	1602(4)	853(5)
C(6)	1334(4)	2158(5)	912(6)
C(7)	1109(4)	2449(5)	334(6)
C(8)	1197(4)	2176(6)	−285(6)
C(9)	1513(4)	1628(5)	−355(5)
C(10)	2850(4)	892(4)	−151(4)
C(11)	2913(4)	1316(4)	−685(5)
C(12)	3442(5)	1521(5)	−881(6)
C(13)	3905(5)	1292(5)	−554(6)
C(14)	3848(4)	868(6)	−16(6)
C(15)	3319(4)	675(5)	187(5)
C(16)	1858(4)	150(4)	−525(4)
C(17)	1281(5)	24(5)	−486(5)
C(18)	1025(7)	−388(6)	−950(6)
C(19)	1360(7)	−681(6)	−1459(8)
C(20)	1904(7)	−553(6)	−1512(7)
C(21)	2162(6)	−123(5)	−1051(5)
C(22)	1615(4)	−490(4)	1724(4)
C(23)	1194(4)	−39(5)	1718(5)
C(24)	753(4)	−83(5)	2171(5)
C(25)	742(4)	−581(5)	2636(5)
C(26)	1146(4)	−1044(5)	2634(5)
C(27)	1581(5)	−1002(5)	2198(5)
C(28)	2811(4)	−477(5)	1744(5)
C(29)	3085(5)	−1066(7)	1854(6)
C(30)	3504(6)	−1107(8)	2338(6)
C(31)	3648(5)	−571(8)	2701(7)
C(32)	3390(5)	21(7)	2597(6)
C(33)	2970(4)	52(6)	2112(5)
C(34)	2240(4)	−1059(4)	581(4)
C(35)	1772(5)	−1393(5)	415(6)
C(36)	1787(6)	−1840(6)	−123(7)
C(37)	2274(6)	−1929(6)	−474(7)
C(38)	2746(6)	−1603(5)	−304(6)
C(39)	2729(5)	−1147(5)	216(5)
C(40)	6085(3)	2083(4)	2952(4)
C(41)	6281(4)	2176(5)	2310(4)
C(42)	6853(4)	2200(5)	2182(6)
C(43)	7224(4)	2141(5)	2688(6)
C(44)	7041(4)	2074(5)	3352(7)
C(45)	6471(3)	2039(5)	3490(5)
C(46)	5165(3)	1287(3)	3432(4)
C(47)	5465(4)	760(4)	3214(4)
C(48)	5306(5)	147(4)	3398(5)
C(49)	4852(4)	45(5)	3801(5)
C(50)	4552(4)	563(5)	4015(6)
C(51)	4696(3)	1186(4)	3831(4)
C(52)	5245(3)	2642(3)	3825(3)
C(53)	5304(3)	2453(4)	4513(3)
C(54)	5241(3)	2918(5)	5022(4)
C(55)	5125(3)	3539(5)	4861(4)
C(56)	5078(4)	3732(4)	4183(4)
C(57)	5130(3)	3285(4)	3669(4)

(*continued*)

TABLE 6. (*continued*)

were obtained by least-squares refinement of the θ values of 30 accurately measured reflections (with θ in the range 22–37°). Data were collected at room temperature on a Siemens AED single-crystal diffractometer using nickel-filtered Cu Kα radiation ($\lambda = 1.54178$ Å) and the $\theta/2\theta$ scan type. All reflections with θ in the range 3–65° were measured; of 9027 independent reflections, 3476, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analyzed according to Lehmann and Larsen [24]. The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.127 and 0.879) [25].

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters for all the non-hydrogen atoms. The ΔF map also revealed the presence in the crystal of a water molecule. All hydrogen atoms, excepting those of the water molecule, were placed at their geometrically calculated positions (C–H = 1.08 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $K = 0.598$ and $g = 0.0088$ at convergence. Final R and R' values were 0.0589 and 0.0649, respectively. The SHELX-76 and SHELXS-86 systems of computer programs were used [26]. Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 27. Final atomic coordinates for the non-hydrogen atoms are given in Table 6. All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Supplementary material

Additional data available from the Cambridge Crystallographic Data Centre comprise coordinates of the hydrogen atoms, thermal parameters and a complete list of bond distances and angles.

Acknowledgements

This work has been supported by M.U.R.S.T. and by C.N.R., Rome.

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