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# Cyanide bridged trinuclear complexes with Fe–CN–$MCl_2$–NC–Fe backbones (M = Ni, Cu, Zn)

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

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**Abstract**

The title complexes were prepared from Cp(dppe)Fe–CN and the metal chlorides. Cp(dppe)Fe–CN–Cu–Cl and Cp(dppe)Fe–CN–$CuCl_2$–NC–Fe(dppe)Cp were characterised by structural determination. Electrochemical measurements have shown that there is no electronic interaction between the two outer iron centres in the $NiCl_2$ and $CuCl_2$ derived complexes. The $ZnCl_2$ derived complex, however, shows two separate redox waves that allows us to assign the mono-oxidised species as a class II mixed valent species according to the classification of Robin and Day. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Trinuclear complexes; Cyanide bridging; Electrochemistry; Metal–metal interactions; Structure

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## 1. Introduction

In recent years there has been an upsurge of activity in the field of polynuclear or polymeric metal cyanides which have been found usable for materials with electrical conductivity, high magnetic moments and photophysical properties [1–3]. We became attracted to this field through the synthetic features offered by it. In a recent review we have outlined the challenges that, in our opinion, are presented by this class of compounds [4]. It seems to us that a systematic synthetic approach is warranted to systems with arrays of $L_nM$ building blocks and bridging CN ligands. This approach should help to evaluate the factors governing electronic interactions along the $(M–CN)_x$ chains, like the nature and oxidation state of the $L_nM$ units, the geometry at the interconnected metal atoms, and the orientation (cyanide/isocyanide) of the bridging CN ligands.

So far we have addressed these questions by a comprehensive study of dinuclear complexes [5] and by investigations of trinuclear complexes with square-planar, tetrahedral and octahedral $L_nM$ units in the centre [6–8]. Previously, our central $L_nM$ units were classical or organometallic complexes whose choice was dictated by the necessity to use substitution-inert species in order to avoid isomerisations or dismutations. The recent discovery by Connelly et al. [9–11] that quite inert trinuclear complexes are also accessible with simple metal ions or metal halides at the centre, i.e. that cyanometalates are good ligands for $M^+$ or $MCl_2$, has prompted us to extend our studies to these central units as well. For a first comparative study we chose $NiCl_2$, $CuCl_2$ and $ZnCl_2$, which allow for the evaluation of the effects of tetrahedral (Ni, Zn) versus square-planar (Cu), redox-active (Ni, Cu) versus non redox-active (Zn), and paramagnetic (Ni) versus diamagnetic (Zn) metal ions in an otherwise identical $(L_nM'–CN)_2MCl_2$ environment. As the $L_nM'$–CN ‘ligand’ we chose Cp(dppe)Fe–CN, which we had found to be most suitable for one-electron oxidations. Thus, the compounds to be studied were **1a**–**c**.

Cp(dppe)Fe–CN–$MCl_2$–NC–Fe(dppe)Cp

**1a**: M = Ni, **1b**: M = Cu, **1c**: M = Zn

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## 2. Preparations

The reactions were straightforward. Combining the hydrated metal salts and Cp(dppe)Fe–CN in methanol or acetonitrile at room temperature produced the three complexes **1**. Although IR spectra of the reaction solutions of **1a** and **1c** (only one ν(CN) band) indicated that there is only one product in solution, the isolated yields were low, which is mostly due to the high solubility of the compounds. In the case of **1b**, the ligation of $CuCl_2$ by Cp(dppe)Fe–CN is accompanied by a redox reaction reminiscent of that between copper salts and cyanide. As a result, the copper(I) complex **2** was isolated in a better yield than **1b**.

Cp(dppe)Fe–CN–Cu–Cl (**2**)

The colour of the nickel complex **1a** (dark green) was an indication of its tetrahedral and, hence, paramagnetic nature, which was then verified by NMR spectroscopy. On the other hand, the linear and diamagnetic nature of the copper(I) complex **2** was verified by its NMR spectrum, as were the paramagnetism of **1b** and the diamagnetism of **1c**.

The ν(CN) bands in the IR spectra of the complexes are listed in Table 1. They are quite similar for the three complexes **1**, which is surprising when considering the very different electronic and geometrical situations. However, the ν(CN) bands of complexes *cis*-$PtL_2[NC–Fe(dppe)Cp]_2$ [7] are also located at practically the same positions. Thus, it must be concluded that for these compounds it is predominantly the divalent nature of the metal attached at the nitrogen atom of Cp(dppe)Fe–CN and not its electronic situation that causes the observed effects. As discussed previously [5,7], the metal–nitrogen interaction in the M–N≡C–M′ bridge is, in essence, a σ-bond. The electron withdrawal from the $CN^-$ ligand caused by it is compensated by enhanced π-backdonation from the C-bound metal. In the cases discussed here this balance of σ-donation from the N atom and π-backdonation to the C atom seems to be always the same. For complex **1b** with a linear NC–Cu–CN arrangement, one would have expected only one ν(CN) band, but the distortions of its symmetry (see below) seem to be sufficient to allow for the appearance of the (weaker) second band. Complex **2** has its ν(CN) band in a region that has also been observed before for dinuclear derivatives of Cp(dppe)Fe–CN [7].

Table 1
ν(CN) IR data (in KBr, $cm^{-1}$)

| | | |
|---|---|---|
| **1a** | 2086s | 2068s |
| **1b** | 2091s | 2068m |
| **1c** | 2088s | 2057s |
| **2** | 2080s | |

## 3. Structures

The copper complexes **1b** and **2** formed crystals suitable for a structure determination. The resulting structures confirmed the expectations, i.e. a linear coordination of copper in **2** and a square-planar trans configuration in **1b**. Figs. 1 and 2 show the molecular structures, while Table 2 lists bond lengths and angles. In both cases one Cp(dppe)Fe–CN ‘ligand’ describes the molecular details, as complex **1b** has the central copper ion on a crystallographic inversion centre.

The structures show the Cp(dppe)Fe–CN units to be suitable ligands for CuCl and $CuCl_2$, as the geometries at copper and the copper–chlorine distances are very close to those in CuCl·tetramethylpiperidine [12] and $CuCl_2$·2 cystosine [13], while the copper–nitrogen distances in **1a** and **2** are about 0.1 Å shorter than in the reference compounds due to the smaller radius of the sp-configured nitrogen. In **2** the copper ion is in an almost ideally linear, and in **1b** in an almost ideally square-planar ligand environment. The characteristically different radii of Cu(I) and Cu(II) are reflected in the Cu–Cl and Cu–N distances, which differ by 0.2 and 0.1 Å, respectively. It is noticeable that **2**, unlike most CuCl adducts with nitrogen bases, is monomeric although there is no steric hindrance near the Cu–Cl unit.

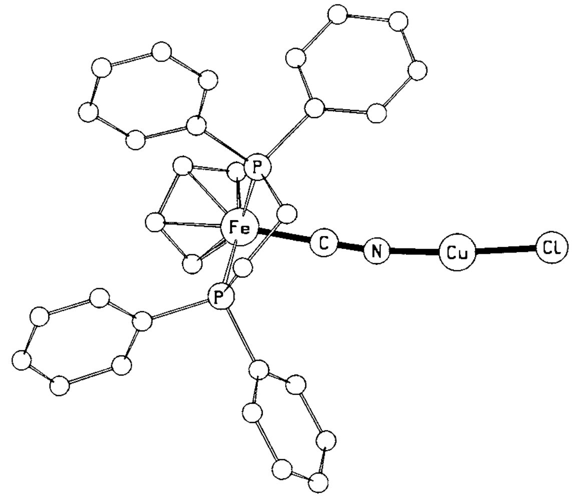

Fig. 1. Molecular structure of complex **2**.

The bonding features of the Fe–C–N units are as observed before [7]. The π-backdonation from iron to cyanide causes a close-to-linear array of Fe, C, and N. The spread of the C–N bond lengths, as always, it too small to be useful for any conclusions. On the other hand, the large difference of the Cu–N bond lengths between **2** and **1b** is so clearly caused by the difference in coordination numbers that any electronic influence is obscured. However, the considerable deviation of the Cu–N–C arrays in both complexes from linearity is an indication of the absence or small magnitude of any π-interaction between copper and the cyanide ligands.

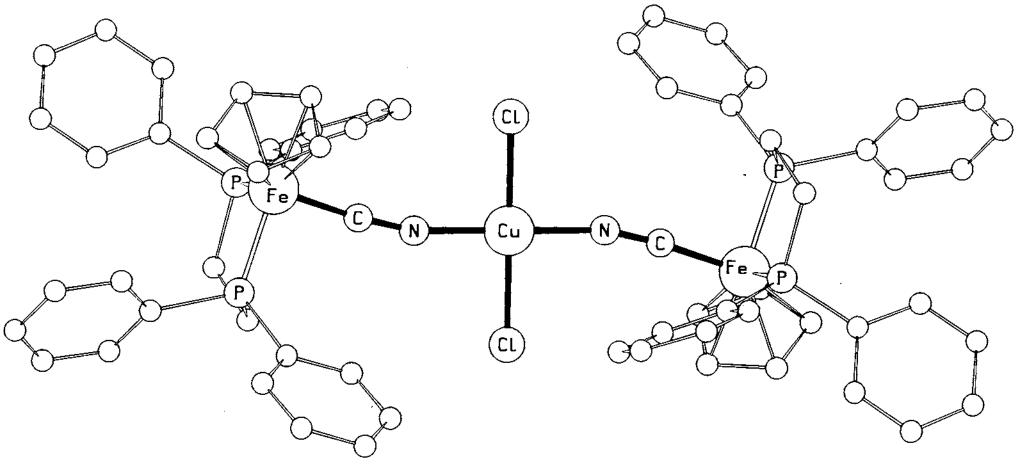

Fig. 2. Molecular structure of complex **1b**.

Previously described systems with cyanide bridging between iron and copper include (porphyrin)Fe–(μ-CN)–Cu(tripod) complexes [14] and the star-like $[Fe\{CN–Cu(tripod)\}_6]^{8+}$ ion [15]. While their ligand environment at copper is quite different from that in **1b** or **2**, their Fe···Cu, Fe–C, and Cu–N distances compare well with those reported here. When they contain the Fe–C–N–Cu sequence, they also show the typical bending at the nitrogen atom with Cu–N–C angles between 163 and 175°.

Table 2
Bond lengths (Å) and angles (°) in complexes **2** and **1b**

| | **2** | **1b** |
|---|---|---|
| Fe···Cu | 4.816(1) | 4.867(1) |
| Cu–Cl | 2.079(2) | 2.303(1) |
| Cu–N | 1.806(4) | 1.909(4) |
| C–N | 1.169(5) | 1.156(6) |
| Fe–C | 1.859(5) | 1.860(4) |
| Cl–Cu–N | 176.2(1) | 90.6(1) |
| Cu–N–C | 170.9(4) | 166.8(4) |
| Fe–C–N | 178.2(4) | 173.1(4) |

## 4. Redox behaviour

All four complexes could be subjected to cyclic voltammetry in dichloromethane solution, and in each case the electron-rich Cp(dppe)Fe centre could be identified as the one that is oxidised first. In no case was a reduction observed down to −0.4 V vs. Ag/AgCl.

In the cases of the nickel complex **1a** and the copper(I) complex **2**, the voltammetric responses were not clean. For **1a** very high scan rates ($>1$ V $s^{-1}$) had to be applied to observe reversible one-electron oxidations at ca. +0.50 V. For **2** a reversible one-electron oxidation at +0.72 V could only be observed if the scan was reversed at +0.8 V. Beyond 0.8 V a second oxidation took place, which is irreversible and caused coating of the electrode. The redox potentials in the range 0.4–0.7 V are characteristic of Cp(dppe)Fe in a cyanide-bridged situation [5–8]. The irreversibility of the redox processes for **1a** and **2** points to the fact that these simple classical complexes are more labile than the previously investigated ones derived from Pt(II) or organometallic centres. After oxidation, either at iron or copper, this lability is increased and obviously causes the oxidised complexes $[\mathbf{1a}]^{2+}$ and $[\mathbf{2}]^{2+}$ to disintegrate.

In contrast, the cyclic voltammogram of **1b** (see Fig. 3) displays two waves representing three reversible one-electron oxidations. The first, large wave at 0.46 V corresponds to oxidation at both iron centres. It is somewhat broadened, but shows no indication of two peaks, not even in the square wave voltammogram. The second wave at 0.71 V can be assigned to a Cu(II)/Cu(III) redox process. It is astonishing that the resulting highly oxidised complex $[\mathbf{1b}]^{3+}$ seems to be stable on the electrochemical time scale (scan rate 100 mV $s^{-1}$). Although the voltammogram gives no indication of an electronic interaction between the two iron centres, the spin state of $[\mathbf{1b}]^{3+}$ should warrant an investigation, which was hampered so far by the low yield of **1b**.

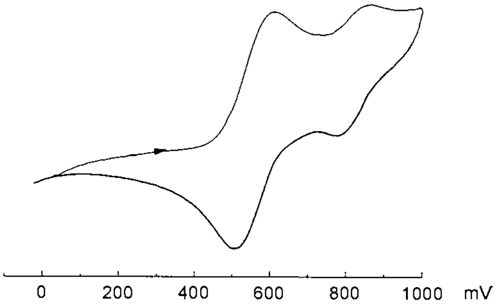

Fig. 3. Cyclic voltammogram of complex **1b**.

The zinc complex **1c**, which has the simplest electronic situation due to the diamagnetism and redox-inertness of the $d^{10}$ ion $Zn^{2+}$, yielded the most informative cyclic voltammogram (see Fig. 4). The only redox events are the separate one-electron oxidations of the two iron centres at 0.63 and 0.75 V, which are similar to the ones observed by Connelly et al. [11] for a $ZnCl_2$ complex with cyanomanganese 'ligands'. They clearly indicate that there is an electronic communication between the two iron units across the tetrahedral $d^{10}$ centre. The magnitude of this interaction, as measured by the separation of the redox steps, is such that the mono-oxidised complex [**1c**]$^+$ can be classified as a mixed valent compound of class II according to the classification of Robin and Day [16]. Its mixed valent nature should go along with an optically induced metal–metal charge transfer observable in the NIR spectrum [7]. Attempts to verify this for **1c** and similar complexes are the subject of our ongoing investigations in this field.

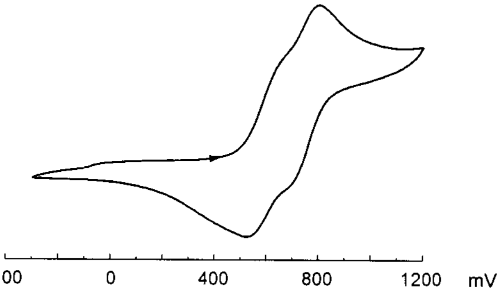

Fig. 4. Cyclic voltammogram of complex **1c**.

Having used the Cp(dppe)Fe–CN 'ligand' for a variety of trinuclear complexes of the type Cp(dppe)-Fe–CN–$ML_n$–NC–Fe(dppe)Cp and having recorded their cyclic voltammograms [6–8], we can make comparative statements on the suitability of the central $ML_n$ units to facilitate electronic communication between the peripheral iron centres. A splitting of the redox waves was observed for $ML_n$ = *trans*-$L_2$Pt(II), *cis*-(bipy)$_2$Fe(II), Cp(CO)Fe, *trans*-(salen)Fe(III), and $ZnCl_2$. No splitting was observed for *cis*-$L_2$Pt(II), $NiCl_2$, and *trans*-$CuCl_2$. Thus, among the octahedral complexes both cis and trans arrangements are favourable, among the square-planar complexes both cis (Pt) and trans (Cu) configurations can be unfavourable, and among the tetrahedral complexes only the diamagnetic ones seem to be favourable. This is not very systematic, and clearly further investigations are necessary to gain a better understanding.

## 5. Experimental

The general experimental and measuring techniques are given in Ref. [7].

### 5.1. Complex **1a**

A 20 mg (0.08 mmol) sample of $NiCl_2 \cdot 6H_2O$ and 90 mg (0.16 mmol) of Cp(dppe)Fe–CN in 30 ml of methanol were stirred for 30 min. After evaporation to dryness in vacuo the residue was picked up in 5 ml of dichloromethane and layered with 10 ml of petroleum ether (b.p. 60–70°C). After 2 days 10 mg (5%) of **1a** (m.p. > 300°C) had separated as dark green needles, which were freed from the liquids by a syringe and dried in vacuo.

Anal. Found: C, 60.19; H, 4.71; N, 2.13. $C_{64}H_{58}Cl_2Fe_2N_2NiP_4 \cdot CH_2Cl_2$ (1220.36 + 84.93). Calc.: C, 59.81; H, 4.63; N, 2.15%.

### 5.2. Complexes **1b** and **2**

A 160 mg (0.29 mmol) sample of Cp(dppe)Fe–CN in 20 ml of acetonitrile was added to a stirred solution of 25 mg (0.14 mmol) of $CuCl_2 \cdot 2H_2O$ in 20 ml of acetonitrile. After stirring for 1 h, the volume was reduced in vacuo until a yellow–brown precipitate formed. This was filtered off and washed with three 5 ml portions of acetonitrile. The remaining residue was dissolved in 5 ml of dichloromethane and layered with 10 ml of diethyl ether. After 2 days 2 mg (0.5%) of **1b** had separated as dark green needles, m.p. 300°C (dec.), which were freed from the liquids with a syringe and washed with diethyl ether.

Anal. Found: C, 59.76; H, 4.37; N, 2.04. $C_{64}H_{58}Cl_2CuFe_2N_2P_4 \cdot CH_2Cl_2$ (1225.22 + 84.93). Calc.: C, 59.59; H, 4.62; N, 2.14%.

The filtrate from the reaction solution was evaporated to dryness in vacuo and subjected to chromatography with a 5:3 mixture of dichloromethane/acetone over a 2 × 20 cm silica gel column affording a single yellow band. After evaporation to dryness the material was picked up in 5 ml of acetone and layered with 20 ml of diethyl ether. After 1 day 20 mg (11%) of **2** had separated as yellow plates, m.p. 225°C (dec.), which were freed from the liquids with a syringe and washed with diethyl ether.

Anal. Found: C, 58.68; H, 4.47; N, 2.08. $C_{32}H_{29}ClCuFeNP_2$ (644.38). Calc.: C, 59.65; H, 4.54; N, 2.17%. $^1$H-NMR (acetone-$d_6$): $\delta = 7.75–7.19$ (m, 20H, Ph), 4.33 (s, 5H, Cp), 2.50–2.42 (m, 4H, $C_2H_4$).

### 5.3. Complex **1c**

Complex **1c** was synthesised using the same procedure employed for **1a** except 11 mg (0.08 mmol) of $ZnCl_2 \cdot 6H_2O$ and 90 mg (0.16 mmol) of Cp(dppe)Fe–CN were used. Yield: 20 mg (5%) of **1c** as dark green needles, m.p. > 300°C.

Anal. Found: C, 59.69; H, 4.57; N, 2.08. $C_{64}H_{58}Cl_2Fe_2N_2P_4Zn \cdot CH_2Cl_2$ (1227.06 + 84.93). Calc.:

C, 59.51; H, 4.61; N, 2.14%. $^1$H-NMR (acetone-$d_6$): $\delta = 8.56–7.16$ (m, 20H, Ph), 5.65 (s, 5H, Cp), 1.52 (m, 4H, $C_2H_4$).

### *5.4. Crystal structure determination*

Crystals were obtained directly from the isolated compounds. The data sets were obtained with an Enraf–Nonius CAD4 diffractometer using Mo–$K_\alpha$ radiation and the $\omega/2\theta$ scan technique at $2\theta = 4–52°$. Absorption corrections, based on $\Psi$-scans, were applied. The structures were solved by direct methods and refined anisotropically using the SHELX program suite [17]. Hydrogen atoms were included with a common isotropic temperature factor and a fixed C–H distance of 0.96 Å. The $R$ values are defined as $R_1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR_2 = \Sigma\{w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{0.5}$. Drawings were produced with SCHAKAL-97 [18]. Table 3 lists the crystallographic details.

Table 3
Crystallographic details for complexes **1b** and **2**

| | **1b** | **2** |
|---|---|---|
| Crystal size (mm) | $0.2 \times 0.1 \times 0.5$ | $0.25 \times 0.15 \times 0.01$ |
| Space group | $P2_1/m$ | $P2_1/c$ |
| $a$ (Å) | 13.196(3) | 10.128(3) |
| $b$ (Å) | 14.345(3) | 16.200(5) |
| $c$ (Å) | 15.771(3) | 18.741(7) |
| $\beta$ (°) | 102.37(3) | 103.48(4) |
| $Z$ | 2 | 4 |
| $V$ (Å$^3$) | 2916.1(2) | 2990.0(2) |
| $D_{calc}$ (g cm$^{-3}$) | 1.49 | 1.43 |
| $\mu$ (mm$^{-1}$) | 1.19 | 1.42 |
| No. reflections collected | 5980 | 18837 |
| No. independent reflections [$I > 2\sigma(I)$] | 4412 | 2232 |
| Variables | 367 | 343 |
| $R_1$ | 0.050 | 0.040 |
| $wR_2$ | 0.141 | 0.072 |
| Residual electron densities (e Å$^{-3}$) | +0.7, −0.8 | +0.3, −0.3 |

## 6. Supplementary material

The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre under the reference numbers 117167 (for **2**) and 117166 (for **1b**). Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Telefax: +44-1223-336033; e-mail: teched@chemcrys.cam.ac.uk).

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