

# A highly redox-active tetranuclear complex with a nearly linear Fe–CN–Mn–O–Mn–NC–Fe backbone<sup>1</sup>

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## Abstract

The purple complex [Cp(dppe)Fe–CN–MnPc]<sub>2</sub>O is obtained from Cp(dppe)Fe–CN and MnPc upon spontaneous oxidation as a Cp(dppe)Fe–CN solvate. Its crystal structure shows a close-to-linear array of atoms along the Fe–CN–Mn–O–Mn–NC–Fe backbone of the tetranuclear complex with an Fe–Fe distance of 13.2 Å. The cyclic voltammogram shows six redox waves for the complex of which two are assignable to the Fe(II)/Fe(III) couples, two to redox changes of manganese, and two to reductions of the phthalocyanine rings. © 1997 Elsevier Science S.A.

## 1. Introduction

The electron transfer capability of the cyanide ion linking two transition metal centers is most visible and well-investigated for Prussian Blue and related solid state compounds. In recent years it has also been exploited for charge transfer properties of di- and trinuclear coordination compounds containing M–CN–M' units (for recent reviews see Ref. [1]), and evidence for remote intervalence transfer in trinuclear systems [2] and electrical conductivity in M–CN–M polymers [3] has been obtained.

We became interested in this field through our work on the linking of redox-active organometallic units to metal carbonyl clusters [4]. We then found that the use of such organometallic units (rather than classical coordination compounds) in heterometallic M–CN–M' systems offers the advantage of intrinsecity, allowing a systematic study of M–CN–M'/M–NC–M' linkage isomerism and its consequences for the electronic properties of the CN-linked complexes as well as the isolation and full characterization of the corresponding one-electron oxidation compounds [5].

As an extension of this work we intended to couple

organometallic units via the CN link to coordination compounds with redox-active ligands. As such we chose porphyrin and phthalocyanine complexes of the first row transition metals. Our expectations in terms of a rich electron transfer chemistry were confirmed [6], but we also found some unexpected results. This paper reports one of the latter, the spontaneous formation of an Mn–O–Mn bridged double-decker complex bearing cyanide linked organoiron units as axial ligands.

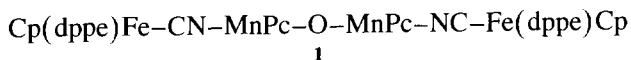
## 2. Results and discussion

The reaction of manganese(II) phthalocyanine (MnPc) with an excess of the cyanoiron complex Cp(dppe)Fe–CN (dppe = bis(diphenylphosphido)ethane) in toluene produces the tetranuclear complex **1** in good yields. This reaction involves coordination of one Fe–CN unit to each manganese and the incorporation of oxygen with concomitant oxidation of manganese to Mn(III). The oxidation occurs even in carefully (though not extremely) degassed solvents. We assume that the attachment of the strongly electron-donating Cp(dppe)Fe–CN 'ligands' significantly increases the susceptibility of the Mn(II) centers to oxidation, as has been previously observed upon attachment of pyridine ligands [7]. Complex **1** crystallizes with two equivalents of Cp(dppe)Fe–CN which we have not yet been able to remove by recrystallization or to avoid by changing the reaction

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<sup>1</sup> Dedicated to Professor Dr. G. Huttner on the occasion of his 60th birthday.

conditions. In this respect, **1** is again similar to the previously reported complex  $(\text{py} \cdot \text{MnPc})_2\text{O} \cdot 2\text{py}$  [7].



Complex **1** is characterized by a  $\nu(\text{CN})$  band in the IR at  $2075\text{ cm}^{-1}$  which is shifted by  $10\text{ cm}^{-1}$  to higher wavenumbers in comparison to that of  $\text{Cp}(\text{dppe})\text{Fe}-\text{CN}$ . This is consistent with our observations on dinuclear complexes containing the  $\text{Cp}(\text{dppe})\text{Fe}-\text{CN}$  unit [8], being attributable to a strengthening of the C–N bond by withdrawal of electrons on the nitrogen side. The Soret band in the visible spectrum of **1** is located at 620 nm, identical to that of the above-mentioned pyridine adduct [7] and shifted by  $-60\text{ nm}$  in comparison to that of unsolvated MnPc, in agreement with the oxidation and six-fold coordination of manganese.

The molecular structure of complex **1** is depicted in Fig. 1. The whole molecule has crystallographic C2 symmetry with the oxygen atom located on a two-fold axis. The building blocks  $\text{Cp}(\text{dppe})\text{Fe}$  and MnPc display no unusual features in bond lengths, conformations or relative orientations [5–8]. Molecular fragments of **1**, i.e. the  $\text{Fe}-\text{CN}-\text{M}$  [4–6] or  $\text{PcMn}-\text{O}-\text{MnPc}$  units [7,9] are well known, and linear  $\text{M}-\text{O}-\text{M}$  arrays in bis(porphyrinato) or bis(phthalocyaninato) complexes of transition metals (for molybdenum cf. Ref. [10]; for ruthenium cf. Ref. [11]; for osmium cf. Ref. [12]), specifically iron (for the most recent example see Ref. [13]), have been observed many times before.

Crystal data:  $\text{C}_{204}\text{H}_{160}\text{Fe}_4\text{Mn}_2\text{N}_{20}\text{O}_8$ ,  $M = 3488.56$ , monoclinic, space group  $C2/c$ ,  $Z = 4$ ,  $a = 51.762(2)$ ,  $b = 13.696(2)$ ,  $c = 32.491(2)\text{ \AA}$ ,  $\beta = 128.01(2)^\circ$ ,  $V = 18149.5(30)\text{ \AA}^3$ ,  $d_{\text{calc}} = 1.25\text{ g cm}^{-3}$ ,  $\mu = 4.73\text{ mm}^{-1}$ , Nonius CAD4 diffractometer, Cu K $\alpha$  radiation,  $\theta = 2-60^\circ$ , 9433 independent reflections, 6642 observed reflections ( $I > 2\sigma(I)$ ), 1116 variables,  $R = 0.077$ . The crystallographic data of the structure

were deposited at the Cambridge Crystallographic Data Centre. Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +12 23/3 36 0 33; e-mail: [teched@chemcrys.cam.ac.uk](mailto:teched@chemcrys.cam.ac.uk)).

The molecular backbone of **1**,  $\text{Fe}-\text{CN}-\text{Mn}-\text{O}-\text{Mn}-\text{NC}-\text{Fe}$ , is close-to-linear, showing the largest deviation from  $180^\circ$  at the Mn–N–C angles as observed in other cases before [8,14]. Its extension ( $\text{Fe} \cdots \text{Fe}$  distance) is 13.18 Å, one of the largest so far in structurally characterized cyanide bridged oligonuclear complexes. Its atom sequence is unprecedented. It is obvious that the bonding situation along the molecular backbone allows electronic interactions along the chain between all four of its metallic constituents.

One way of testing such an electronic interaction is redox chemistry and the associated characterization of mixed-valence species. So far we have not been able to isolate oxidized or reduced derivatives of **1**, and spectroelectrochemical studies are still pending. But cyclic voltammetry has revealed a wealth of redox states which can be interconverted reversibly on the electrochemical time scale, see Fig. 2. When interpreting the cyclic voltammogram of **1**, the redox waves for four types of redox-active constituents have to be assigned. The highest of the waves, marked X, results from the co-crystallized  $\text{Cp}(\text{dppe})\text{Fe}-\text{CN}$  molecules which we have not been able to remove yet. It serves as a reference for the  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  transitions of the  $\text{Cp}(\text{dppe})\text{Fe}$  constituents of **1**. We assign waves 4 and 5 to these. The waves at lowest potential, 1 and 2, can be assigned with some certainty to reductions of the phthalocyanine rings [15]. The remaining waves, 3 and 6, are then left for  $\text{Mn}(\text{II})/\text{Mn}(\text{III})$  and/or  $\text{Mn}(\text{III})/\text{Mn}(\text{IV})$  transitions. Their identification is less certain and made difficult by the fact that further waves may be hidden under wave X.

We consider the occurrence of two  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$

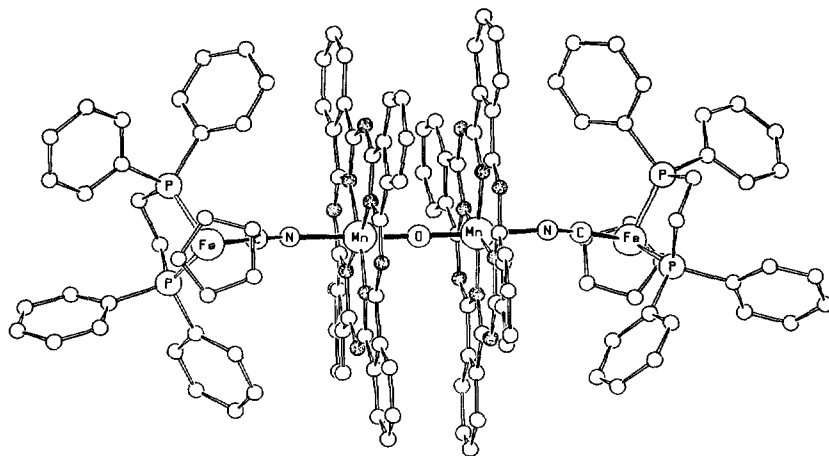


Fig. 1. Molecular structure of **1**. Pertinent bond lengths: Mn–O 1.71(1), Mn–N 2.05(1), Fe–C 1.87(1), Fe–P 2.189(3) Å. Bond angles Mn–O–Mn 177.9(5), O–Mn–N 177.7(2), Mn–N–C 159.6(7), N–C–Fe 172.4(8)°.

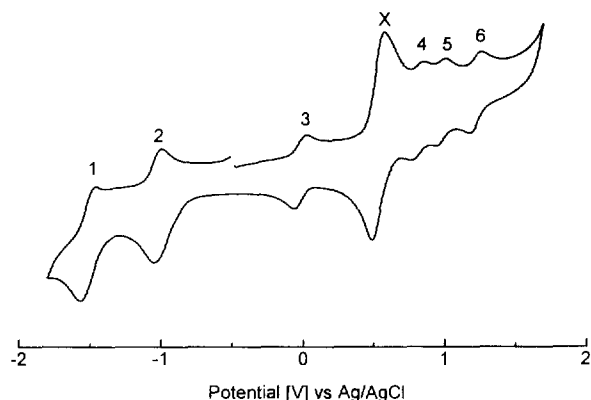


Fig. 2. Cyclic voltammogram of **1** (benzene/acetonitrile 3:1, TBAPF<sub>6</sub> as supporting electrolyte, platinum electrodes, scan rate 500 mV s<sup>-1</sup>).

redox waves the most important piece of information from this study. It indicates that the two iron centers are not independent of each other, i.e. oxidation at one end of the chain exerts an electronic influence changing the redox potential at the other end. This would make the intermediate Fe(II)–Fe(III) species a mixed valence complex of class II and prove that the nine-atom molecular backbone is a conductor for electronic charge.

While this interpretation needs to be corroborated by further physical evidence like IT bands or magnetic interactions, the structure and redox activity of **1** alone show that the Fe–CN–Mn–O–Mn–NC–Fe backbone is a molecular wire with the organic ligands as its insulation. We are working on methods of extending the chain length of this type of complex in the form of isolated and structurally characterized compounds.

### 3. Experimental

**Synthesis of 1:** 500 mg (0.88 mmol) of MnPc and 2.88 g (5.28 mmol) of Cp(dppe)Fe–CN were suspended in 70 ml of dry toluene. The mixture was refluxed for 5 h and then filtered hot to remove unreacted MnPc. Upon storage at –30 °C most of the excess Cp(dppe)Fe–CN was precipitated and filtered off. The filtrate was evaporated to dryness and the residue washed with 20 ml of acetonitrile, 10 ml of ether, 10 ml of petroleum ether (b.p. 30–50 °C) and then dried for an extensive period in vacuo to yield 504 mg (33%) of **1** as a purple powder of m.p. 158 °C. Anal. Found: C, 69.31; H, 4.59; N, 9.06. C<sub>192</sub>H<sub>148</sub>Fe<sub>4</sub>Mn<sub>2</sub>N<sub>20</sub>OP<sub>8</sub> (3332.47) Calc.: C, 69.20; H, 4.48; N, 8.41%. Single crystals were

obtained by slow diffusion of pentane into a benzene solution of **1**. They contain two molecules of benzene per formula unit of **1**.

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