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Electronic structure of a heterotetranuclear Cu$^{I}_{2}$Fe$^{II}_{2}$ complex bridged by w-accepting 2,2′-bipyrimidine. Close-lying but orthogonal frontier orbitals

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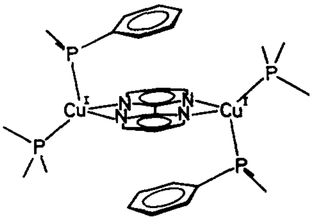
Abstract

The new complex **1** contains two **1,1′-bis(diphenylphosphino)ferrocene-coordinated** copper(I) centers which are connected by the &,-symmetric π acceptor **2,2′-bipyrimidine.** Cyclic voltammetry and ESR reveal a ferrocene-based HOMO and a bpym-centered LUMO. There is no detectable HOMO/LUMO absorption band because of orthogonality between the two types of orbitals. The lack of strong solid-state MLCT luminescence is an indirect consequence of the small bite angle of the **bis(diphenylphosphino)ferrocene** ligand, which **cannot** induce strong distortion at the copper center.

Poly(hetero)metallic complexes which involve electron propagating π systems as bridging ligands are of interest in respect of energy transfer, charge transfer and magnetic exchange interactions **[1,2].** Using the symmetrically dinucleating **2,2′-bi**pyrimidine **(bpym)** ligand as a π acceptor bridge **[3]** for d^{10} fragments $^{+}\mathrm{CuL}_2$, we have recently shown that this acceptor can also engage in intramolecular π interactions with phenyl rings of co-ligands L **[4].**



(1)

We now report the synthesis and electronic structure of a tetrametallic system **1,** which contains two **1,1′-bis(diphenylphosphino)ferrocene-copper(I)** fragments bound to bpym.

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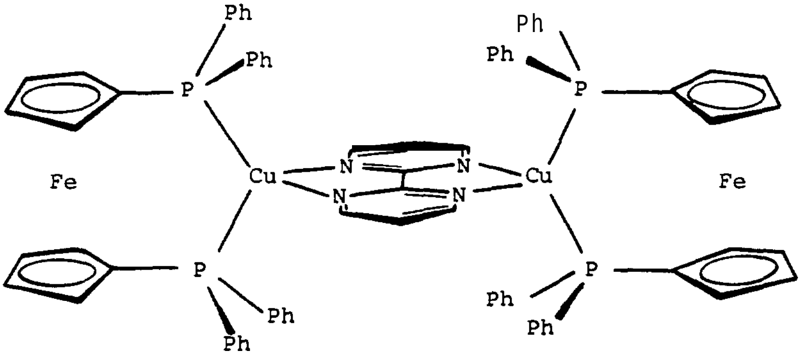
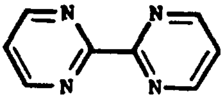


(1)

(2)

bpym:



The previous study on bpym-bridged diphosphanecopper(I) dimers [4] revealed a distorted tetrahedral N_2P_2 arrangement around the copper(I) centers, and the chelating diphosphinoferrocene ligand [5] is thus anticipated to coordinate as depicted in (2). While it was demonstrated that there is a symmetry-allowed charge transfer transition (absorption *and* emission) from the relatively high-lying d_{xz} orbitals of the d^{10} shells [6] of the copper(I) centers to the lowest unoccupied MO (LUMO) [3] of bpym [4], compound **1** contains the even more-electron rich iron(II) centers of ferrocene which might also, albeit indirectly via a second metal [7], interact with the heterocyclic acceptor.

Complex **1**, prepared by established procedures [4], is easily and reversibly reduced at − 1.17 V vs. ferrocene/ferricinium couple as standard in 1,2-dichloroethane/0.1 M Bu_4NPF_6. Oxidation occurs through an initial two-electron step at +0.46 V (resulting in slow dissociation, Fig. 1), and in a second, totally irreversible step at ca. + 1.05 V vs. $Fc/Fc^{+\cdot}$. Similar behaviour was observed in DMF (Fig. 1).

The reduction involves occupation of the π^*(bpym) orbital by one electron, as is evident from a high-resolution ESR spectrum of the singly reduced species (Fig. 2); relatively [8] small $^{63,65}Cu$ (I = 3/2) and ^{31}P (I = 1/2) coupling constants of about 0.65 mT reflect a slight spin delocalization to the metal fragments whereas the $H_{5,5'}$ (0.5 mT) and ^{14}N (I = 1) splitting parameters (0.215 mT) of the bpym ligand indicate the anion radical complex character of the singly reduced complex $\mathbf{1}^{-\cdot}$ [4,9]. The combination of 4 N, 2 H, 2 Cu and 4 P coupling nuclei would in itself lead to a number of 945 theoretical ESR lines, but the high resolution spectrum (Fig. 2) reveals further splitting due to 4 equivalent protons $H_{4,4',6,6'}$ and to three different copper isotope combinations: $^{63}Cu/^{63}Cu$, $^{63}Cu/^{65}Cu$, and $^{65}Cu/^{65}Cu$. The natural abundances are 69% for ^{63}Cu and 31% for ^{65}Cu, and the ratio of nuclear magnetic moments is 1 : 1.07. Full analysis of this system with a theoretical total of 20500 (!) lines has not yet been possible.

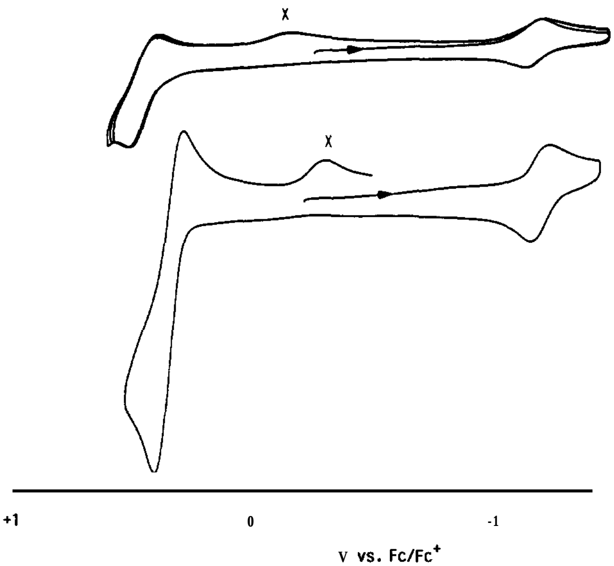


Fig. 1. Cyclic voltammograms of I in 1,2-dichloroethane/0.1 *M* Bu_4NClO_4 (top) and DMF/0.1 *M* Bu_4NPF_6 (bottom). The intensity of the ferrocene oxidation wave and the appearance of an additional peak *x* upon cycling indicate partial decomposition upon oxidation.

The first oxidation involves the two apparently independent ferrocene iron centers at a typical [5b] potential for r-acceptor $((L_nM)Ph_2P-)$ [10] substituted ferrocene, while the irreversible oxidation of the copper(I) centers requires higher potentials. Accordingly, the HOMO-LUMO transition must involve charge transfer from the iron(II) atoms to the bpym ligand, with or without support by the copper centers; the difference of 1.63 V between the oxidation and reduction potentials would translate [11,12] into 1.63 eV = 13150 cm-’ plus Franck–Condon contributions in the order of 0.7 eV = 5600 cm^{-1} [12] for an expected absorption maximum at about 19000 cm-^{1} of the HOMO-LUMO transition. However, the absorption

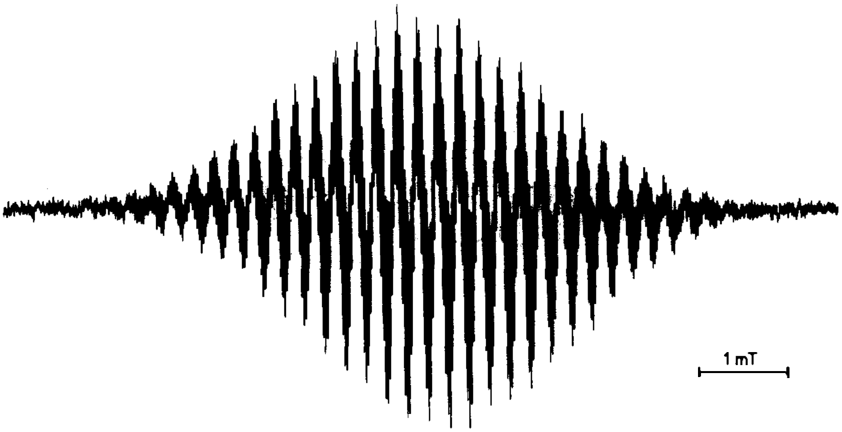


Fig. 2. ESR spectrum of one-electron reduced 1 in dichloromethane/0.1 *M* Bu_4NClO_4 at 300 K (5 μT modulation amplitude).

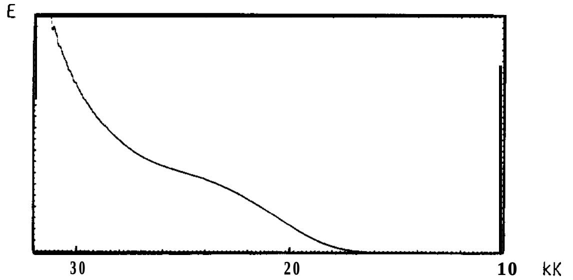


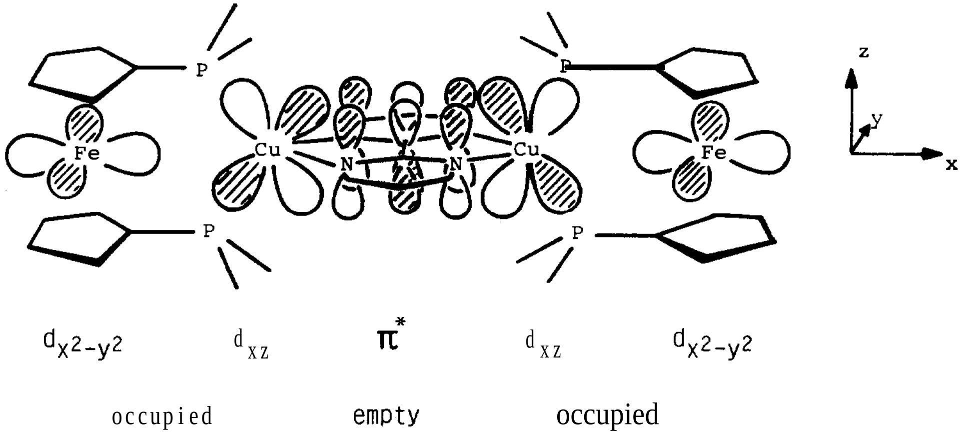
Fig. 3. UV/VIS spectrum of 1 in DMF solution (1 kK = 1000 cm-‘).

spectrum of **1** (Fig. 3), with a shoulder at 24000 cm-’ (MLCT: Cu’ → bpym) [14], is not very different from those of analogous phosphane complexes [4,13] that do not contain ferrocene iron centers.

The reason for the virtual absence of an observable HOMO-LUMO transition lies in the vanishing overlap between the bpym π^* orbital (b_{1u} in D_{2h} symmetry, **FeCuCuFe** on x axis) and the highest (d_{xy}, $d_{x^2-y^2}$) occupied orbitals of a_g and b_{2u} symmetry (bonding combinations) in the ferrocene units [14]; orbital orthogonality (Scheme 1) and the absence of strong spin-orbit coupling are indicated by this result.

Since orthogonality of “magnetic orbitals” usually results in preference for ferromagnetic spin-spin interactions [2c], it should be worthwhile to look at extended paramagnetic systems that make use of the orbital and coordination arrangement employed here.

In agreement with previous observations [4], complex 1 does not exhibit strong luminescence in the solid state because the 1,l’-bis(diphenylphosphino)ferrocene ligand with its P-M-P bite angle of ca. 100” [5], cannot participate [4] in a π interaction (1) between the bipyrimidine acceptor and an electron donating (phosphino)phenyl ring. Only such interactions would lead to a sufficiently distorted copper environment, with an entatic state [15] geometry between Cu’ and $\mathrm{Cu^{II}}$,



Scheme 1

energy minimum configurations which would favour luminescence from an MLCT excited state (Eq. 1) [4].

$$\bullet\,[Cu^{II}(bpym^{-\bullet})Cu^{I}] \rightarrow Cu^{I}(bpym)Cu^{I} + h\nu \qquad (3)$$

Experimental

NMR: Bruker WP 60, TMS as internal standard. ESR: Bruker ESP 300, TMH high sensitivity cavity, intra muros electrolysis in dichloromethane/0.1 *M* Bu_4NClO_4. UV/VIS: Bruins Instruments Omega 10 spectrometer. Luminescence: Perkin-Elmer LB3. Cyclic voltammetry: PAR system 175/273. Three electrode configuration: Ag/AgCl reference, glassy carbon working electrode. Dried 1,2-dichloroethane/0.1 *M* Bu_4NClO_4 or N, N-dimethylformamide(DMF)/O.l *M* Bu_4NPF_6 was used as the electrolyte, and the ferrocene/ ferricinium couple (+ 0.31 V vs. SCE) was used as reference system.

$\{(\mu\text{-}bpym)[Cu(Ph_2P{-}Fc{-}PPh_2)_2]_2\}(BF_4)_2$(1). A suspension of 47 mg (0.75 mmol) of copper powder, 120 mg (0.5 mmol) of copper(II) bis(tetrafluoroborate), 277 mg (0.5 mmol) of l,l'-bis(diphenylphosphino)ferrocene, and 40 mg (0.25 mmol) of 2,2'-bipyrimidine in 25 ml methanol was heated under reflux for 2 h. The solution was allowed to cool and the brownish precipitate was collected and treated with DMF. Remaining copper powder was removed by filtration, and addition of dichloromethane to the filtrate yielded bronze-coloured microcrystals, which were collected, washed with dichloromethane and dried in vacuo. Yield: 219 mg (56%). ^{1}H-NMR (CD_3CN): δ 4.26 (m, 8H), 4.45 (m, 8H), 7.37 (m, 40H), 8.0 (broad m, 2H), 8.9 (d, $J = 8$ Hz, 4H). Anal. Found: C, 57.71; H, 3.94; N, 3.70. $C_{76}H_{62}B_2Cu_2F_8Fe_2N_4P_4$ (1567.64) calcd.: C, 58,23; H, 3.98; N, 3.57%.

Acknowledgements

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