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On the Electronic Structure and Bonding of the Intriguing Mixed Fe^{2+}/Fe^{3+} $[\{Cp(CO)_2Fe\}^tBuPO_2FeCl_2]_2$-Complex

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ABSTRACT: *The structure and bonding of $[\{Cp(CO)_2Fe\}^tBuPO_2FeCl_2]_2$(**2**) have been investigated theoretically and experimentally. The molecular orbitals of **2** have been calculated to investigate the question why this type of complex forms a planar ring system. The electronic configuration of different electronic states, spin polarization, and bonding of **2** are discussed.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:398–405, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20109

INTRODUCTION

The dimer $[\{Cp(CO)_2Fe\}^tBuPO_2FeCl_2]_2$(**2**) (see Scheme 1) containing the novel ferriophosphinato-O,O′ligand is formed by simple oxidation reaction of the PH-functionalized diferrio-phosphonium-salt (**1**) [1]. A plausible reaction mechanism is shown in Eq. (1) in which the balance of electrons and substances is kept. In the first step, the phosphonium cation is oxidized by oxygen under elimination of one ferrio group. In the second step, the monoferriophosphinic acid reacts with the oxidized anion (now Fe(III)) of the educt-salt under self-assembling toward this eight-membered ring system.

The structure of **2** is similar to cyclic tetrametaphosphates and other metal ring systems as the dimeric organosubstituated phosphinato-complexes of transition metals, but in contrast to the latter species forms **2** an almost planar eight-membered ring [2] as demonstrated by an X-ray study.

The deviation from planarity is rather small with dihedral angles P1a–Fe2a–P1b–Fe2b = O1a–O2a–O2b–O2b = 0.00°, O1a–Fe2a–P1b–O1b = 4.66° and O2b–Fe2b–P1b–O2a = 8.68° (Fig. 1). Usually, dimeric organosubstituated phosphinato-complexes of transition metals display a nonplanar structure as proven by X-ray analysis [3].

Structural studies of iron complexes of this type are demanding exercises, both experimentally and computationally. Their experimental study requires special experimental conditions [3], and their computations are difficult due to the size of the iron atom and the ligand system [4]. Most computations so far have been concerned with the iron complexes of small-sized ligand systems.

We found it of interest to investigate the electronic structure and bonding of **2** by ab initio computations. We also intended to investigate the reason for planarity in **2** whether this species is subject to a formal Hückel aromaticity or not.

DISCUSSION

Electronic Configuration

To understand the electronic situation in **2**, it is practical to separate the ring system into four isolated Fe

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Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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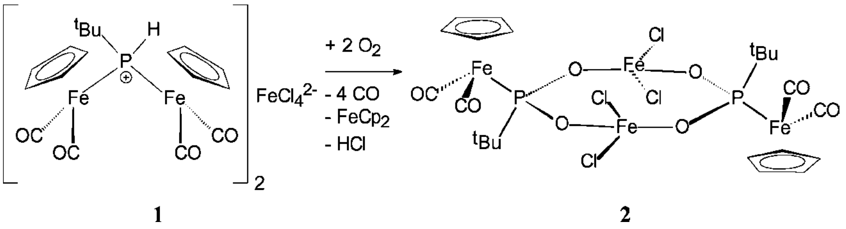


SCHEME 1

centers resulting in formally two "naked" Fe^{2+} and two Fe^{3+} atoms as shown in Fig. 2. The two ring-forming phosphorus ligands can be regarded as a phosphinate (III), $RPO_2{}^{2-}$, system connecting one $CpFe(CO)_2{}^+$ fragment with two $FeCl_2{}^+$ fragments.

Now, each Fe^{3+} center lies in distorted tetrahedral environment (local symmetry is C_{2v}) whereas both Fe^{2+} centers can be regarded as possessing an octahedral ligand arrangement (with Cp^- representing a six-electron donor). Therefore, formally the 3d orbitals of the Fe^{2+} centers split into three t_{2g} and two e_g orbitals resulting in a low-spin t_{2g}^6 configuration. Three electronic configurations are possible for the Fe^{3+} centers in a tetrahedral environment: (i) five unpaired electrons per Fe^{3+} center (high spin case, $e^2t_2^3$) leading to a multiplicity of $M = 11$, (ii) three unpaired electrons and one electron pair ($e^3t_2^2$, $M = 7$), and finally (iii) one unpaired electron (low spin case, $e^4t_2{}^1$) per Fe^{3+} center resulting in a triplet state. Moreover, electronic states with different electronic configurations on both Fe^{3+} centers are possible (e.g. $M = 5$, with one high spin center and one low spin center) but quite unrealistic as this should lead to distortion and therefore different local structures which was not observed in the experiment.

As the energy for spin pairing is rather high and the energy gap in the tetrahedral ligand field between the two e and three t_2 orbitals is fairly small, the high spin case should be the ground state. Indeed, our computations suggest that the high spin configuration (10 unpaired electrons) represents the ground state, indicating the presence of formally two Fe^{3+} (in a tetrahedral environment) and two Fe^{2+} (in an octahedral environment). The high spin configuration was determined by a measurement of the magnetic susceptibility: In agreement with theory, we are able to estimate $\mu = 6.04\ \mu_B$ for each Fe^{3+} center (cf. calculated $\mu = 5.92\ \mu_B$ for $FeCl_4{}^-$)[5] and the Curie temperature $\Theta = -58.44$ K in **2** (see Experimental details). Small differences may stem from small iron oxides impurities on the crystal surface. Through-ring magnetic coupling can be ruled out due to the fairly large distance between the two Fe^{3+} centers ($d(Fe^{3+} - Fe^{3+}) = 4.576$ Å). Experimentally, a linear

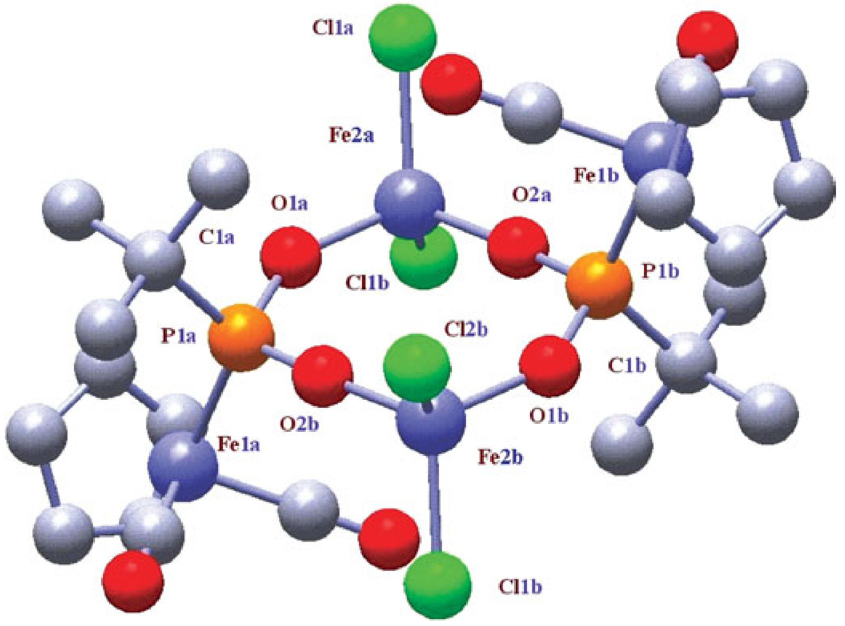


FIGURE 1 Molecular structure and numbering of **2** (color code: blue Fe, red O, green Cl, orange P, gray C).

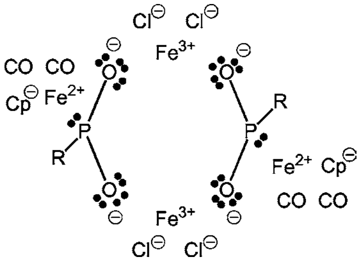


FIGURE 2 Lewis-type representation of **2**.

correlation was found between the magnetic moment and the magnetic field which usually is an indicator for the nonexistence of cooperative effects, e.g. ferromagnetism.

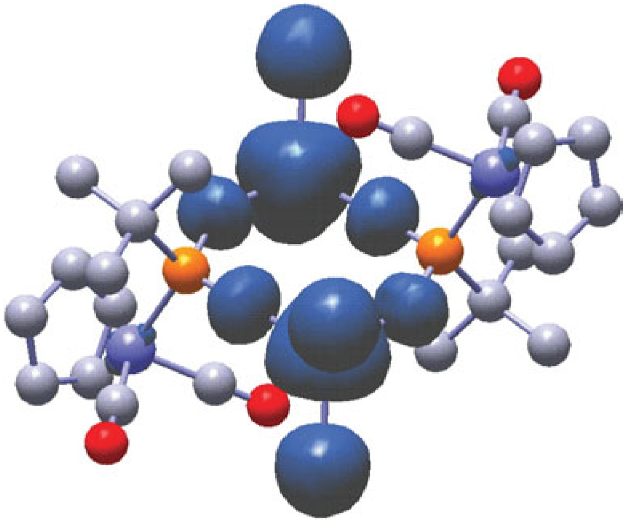


FIGURE 3 α-Spin polarization in **2** with blue color for the corresponding atoms.

Spin Polarization

Spin contamination is an important factor affecting the accuracy of the applied method. The B3LYP density functional method seems to give reasonable unrestricted wave functions with only small amounts of spin contamination (Table 1). The atomic spin densities are summarized in Table 2, and the spin polarization is displayed in Fig. 3 (blue color represents excess of α-spin density). This spin density plot shows the excess of α-spin density delocalized over the Fe^{2+} centers and the entire ligand sphere, the two Cl and two O atoms, with a slightly larger amount of spin density on the Cl atoms (see Table 1). This difference between the oxygen and the chlorine ligands is assumed to be related to the varying electronegativity of the ligand atoms (O: 3.5 vs. Cl: 2.83) [6]. According to the calculated atomic spin densities, only the spin density associated with about four unpaired electrons is found on each of the two Fe^{2+} centers, the rest is localized mostly on the four ligands surrounding the Fe^{2+}. Almost no spin density was found for the Fe^{3+} centers which is in accordance with our consideration on the electronic configuration mentioned in the first section.

To understand the delocalization of the odd electron density over the ligand sphere, we have inspected the molecular orbitals (α-spin MOs and β-spin MOs) of $FeCl_4^-$ which also possesses five unpaired electrons in a tetrahedral environment. Similar to **2**, roughly four unpaired electrons were found on the Fe center and one electron equally delocalized over the four Cl ligands (Table 1). The different factors leading to the delocalization of the five unpaired electrons in tetrahedral iron (3+) complexes are (i) the α-spin electrons in the 3d orbitals are slightly delocalized over the ligands (Figs. 4 and 5); (ii) on the other hand, the 3d orbitals act as acceptor orbitals above all for β-spin electron density leading to a fairly large 3d population which is about 1 for the α-spin electrons (GAP larger than NPA) and much larger than 0 for the β-spin electrons (Figs. 5a and 5b, see Tables 2 and 3). As these two effects do not cancel each other, an excess of α-spin density remains on the ligands; (iii) the population of the 4s orbitals is rather small, and the occupation of the 4p orbitals is negligible (NPA).

Table 2 shows the results of population analyses by the NPA [8] and the Mulliken method. The major difference between the two is in the role of 4p orbitals on Fe; while the Mulliken analysis gives a noticeable 4p contribution, the NPA does not (Table 2). A consequence of this difference is the large difference in the estimated partial charges on the iron center (almost

TABLE 1 Atomic Spin Densities (>0.05) in 2[a]

Species	*Fe2*	*Cl1*	*Cl2*	*O1*	*O2*	*Sum*	*Localization*
2	4.034	0.270	0.282	0.166	0.171	4.923	98.5%
$FeCl_4^-$	4.028	0.243	–	–	–	5.0	100.0%

[a] **2**: 10 unpaired electrons, $M = 2S + 1 = 11$; $<S^2>_{calc} = 30.02351$, shown only the data of one Fe^{3+} center and its ligand sphere (monomeric fragment).

TABLE 2 Natural Population Analysis (NPA) and Gross Atomic Populations (GAP) and Charges of $FeCl_4^-$

Orbital		*Total*	α	β	$(\alpha-\beta)$ *Spin*
4s(Fe)	GAP	0.5825	0.3027	0.2798	0.0229
	NPA	0.4503	0.2296	0.2208	0.0088
$4p_a$(Fe)	GAP[a]	0.2993	0.1538	0.1456	0.0082
	NPA	0.0035	0.0019	0.0015	0.0004
$3d_z^2$(Fe)	GAP	1.2191	1.0387	0.1804	0.8583
	NPA	1.1735	0.9963	0.1772	0.8191
$3d_{xz}$(Fe)	GAP	1.2918	1.0210	0.2708	0.7502
	NPA	1.2620	0.9977	0.2643	0.7334
$3d_{yz}$(Fe)	GAP	1.2918	1.0210	0.2708	0.7502
	NPA	1.2620	0.9977	0.2643	0.7334
$3d_{x^2-y^2}$(Fe)	GAP	1.2191	1.0387	0.1804	0.8583
	NPA	1.1735	0.9963	0.1778	0.8191
$3d_{xy}$(Fe)	GAP	1.2918	1.0210	0.2708	0.7502
	NPA	1.2620	0.9977	0.2643	0.7334
3s(Cl)	GAP	1.9453	0.9732	0.9721	0.0011
	NPA	1.9678	0.9895	0.9782	0.0113
3p(Cl)	GAP	1.7936	0.9369	0.8567	0.0802
	NPA	1.8667	0.9794	0.8873	0.0921
Partial charges		GAP	Fe: $+0.2045e$		
		NPA	Fe: $+1.2972e$		

[a] $a = x.\ y.\ z.$

1e difference). There have been prior warnings about the reliability of the Mulliken analysis especially in molecules with transition metals [8e]. Mulliken populations of all these species displayed for some orbitals quite significant physically unrealistic negative values. As indicated by Weinhold et al. [8e], natural population is found to give a satisfactory description of more ionic species and the dependence on the basis set is much smaller. The results of the NBO analysis are indeed quite robust against changing the basis set. However, as shown by Frenking, "it is important to recognize that a weighting factor automatically disfavors atomic basis functions which are empty in the atomic ground state in the description of the chemical bond. Thus, the NBO method excludes a priori the outermost p orbitals of the TMs from the valence space!" [7].

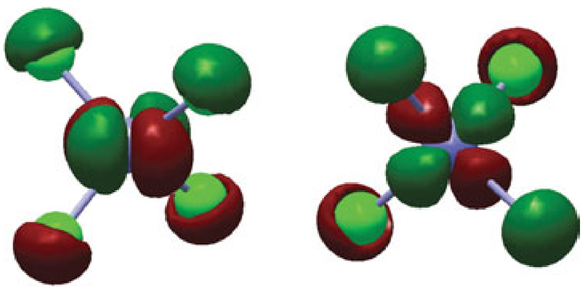
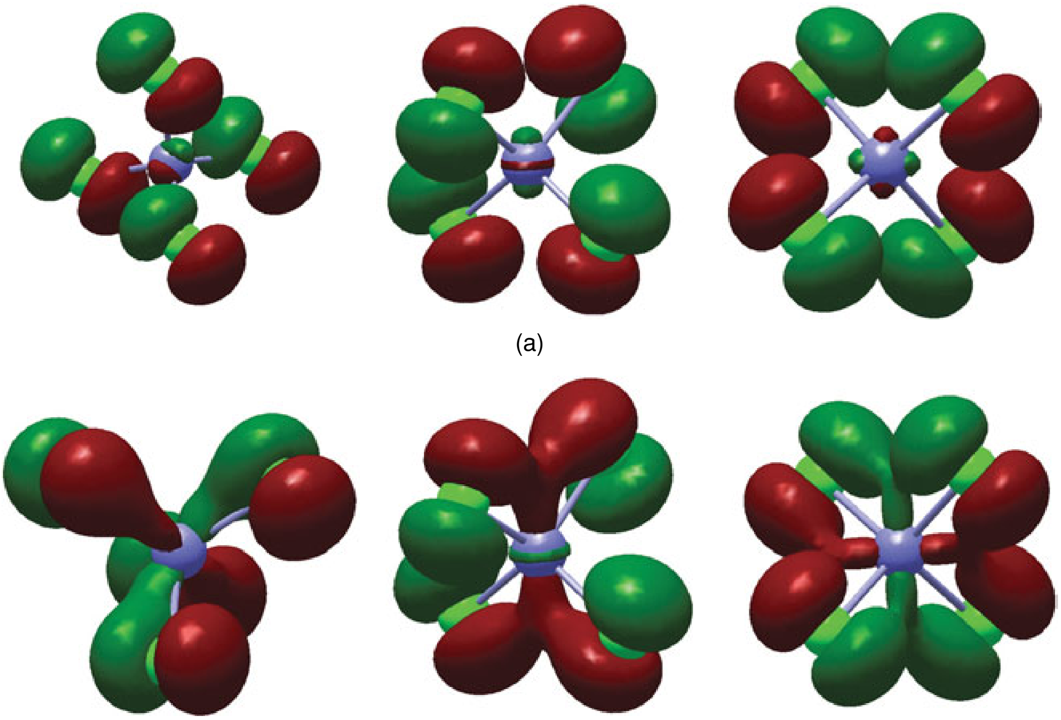


FIGURE 4 Occupied α-spin orbitals showing the partly delocalization of the odd electron density (3d orbitals) over the entire molecule (Cl ligands) in $FeCl_4^-$.

Structure and Bonding

The calculated partial charges of **2** are summarized in Fig. 6. Both iron centers do not represent real Fe^{3+} or Fe^{2+} centers but possess almost the same partial charge with ca. $+0.5\,e$. The Lewis type representation of **2** with ionic bonds between the Fe centers and their ligands alone is certainly not a good description of the bonding in **2**. Resonance between covalent and ionic structures is to be preferred. The P atoms are surrounded by four atoms with fairly short highly polarized P—O bonds indicating bond orders larger than 1.

A striking feature of the molecular structure is the planarity of the eight-membered ring. The dihedral angles are P1a–Fe2a–P1b–Fe2b = O1a–O2a–O2b–O2b = 0.00°, O1a–Fe2a–P1b–O1b = 4.66°, O2b–Fe2b–P1b–O2a = 8.68° over a ring with an average diameter of 4.299 Å. To answer the question why this species is nearly planar, we have investigated the molecular orbitals of **2**. Inspection of the molecular orbitals gave no evidence for a delocalized conjugated π system as it is necessary in a Hückel aromatic system. Instead of having a delocalized conjugated π system, we have found two O—P—O π bond units which are separated by the two Fe^{3+} atoms which do not participate in π bonding (see Fig. 7, Table 3). In the picture of localized two-electron two-centers bonds, the π character arises from the interaction of the oxygen lone pairs with the phosphorous sigma bond system (intramolecular donor acceptor bond, hyperconjugation) [8,9].



(a)

(b)

FIGURE 5 The 3d orbitals on Fe act as acceptors for α- and β-spin electron densities. In the latter case this effect is much larger. (a) Occupied α-spin orbitals showing the partly delocalization of the Cl lone pairs over the 3d orbitals (shown are d_{xy}, d_{z^2} and $d_{x^2-y^2}$) of Fe. (b) Occupied β-spin orbitals showing the partly delocalization of the Cl lone pairs over the 3d orbitals (shown are d_{xy}, d_{z^2} and $d_{x^2-y^2}$) of Fe.

One of the origins of the ring planarity could be this π character of the OPO units. The shape of these molecular orbitals energetically favors the "tetrahedral arrangement" on all Fe centers. A nonplanar ring system would result in a distortion of the local C_{2v} symmetry of the Fe^{3+} centers and the local C_s symmetry of the Fe^{2+} centers as well as the overall C_i symmetry. This distortion could cost energy due to unfavorable electrostatic interaction.

SUMMARY

In the agreement between experiment and theory, we were able to establish that **2** represents a high spin complex with 10 unpaired electrons (five electrons at each Fe^{3+} center). Inspection of the theoretically obtained structural and electronic data revealed that (i) spin polarization results in fairly large delocalization of the odd electron density in the ligand

TABLE 3 Energies of the Calculated π-Type Molecular Orbitals of **2** (see Fig. 7)

No. $^{\alpha}$*MO*	*E* ($^{\alpha}$*MO*) *(a.u.)*	*No.* $^{\beta}$*MO*	*E* ($^{\beta}$*MO*) *(a.u.)*	*Description with Respect to the OPO Unit*
198	−0.25915	188	−0.25932	HOMO; antibonding MO; stabilized by bonding P–C and P–Fe interaction
197	−0.26268	187	−0.26111	HOMO-1; antibonding MO; stabilized by bonding P–C and P–Fe interaction; inversion of the orbital signs on one side due to C_i symmetry
172	−0.33816	161	−0.35169	Nonbonding MO; Lone pair character for O
166	−0.36174	158	−0.35569	Nonbonding interaction MO; Lone pair character for O; Inversion of the orbital signs on one side due to C_i symmetry*
164	−0.39102	154	−0.39514	Bonding MO; Inversion of the orbital signs on one side due to C_i symmetry*
163	−0.39641	153	−0.39677	Bonding MO

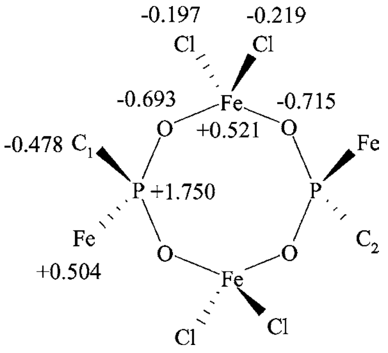


FIGURE 6 Calculated Partial Charges in **2** (NPA).

sphere of both Fe^{3+} centers; (ii) OPO moieties within the eight-membered ring introduce some π character but **1** is no Hückel type system; (iii) the planarity of the eight-membered ring arises due to symmetry and steric effects.

COMPUTATIONAL DETAILS

At first single point computations on the X-ray molecular structure were carried out at the Hartree–Fock level. Different electronic states have been checked. The quadratic convergence SCF procedure was applied to get reliable wave functions. The UHF wave function was then used as initial guess in the following study using density functional theory applying the B3LYP method. B3LYP includes a mixture of Hartree–Fock exchange with DFT exchange-correlation. Becke's three parameter functional where the nonlocal correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used which is implemented in Gaussian 98 [10]. For a concise definition of the B3LYP functional, see [11].

Pseudopotential techniques were used for Fe and a standard 6-31G(d) basis set for Cl, O, P, C, and H (STO-5G). A multielectron adjusted quasi-relativistic effective core potential covering 10 electrons and (8s7p6d1f)/[6s5p3d1f]-GTO valence basis set of the Stuttgart group was used for iron [12].

Mulliken population analyses and NBO analyses [8] were carried out to investigate the bonding in both molecules at the B3LYP level.

EXPERIMENTAL SECTION

Preparation of **2**: A solution of 140 mg (0.12 mmol) **1** in 12 mL of acetonitrile was held for about 2 weeks in air atmosphere. After this period, small prismatic deep purple red single crystals of **2** separated at the bottom of the vessel. They were isolated by decantation of the solution. In the mother liquor some of product **2** still remained which, however, could not be separated as a pure product.

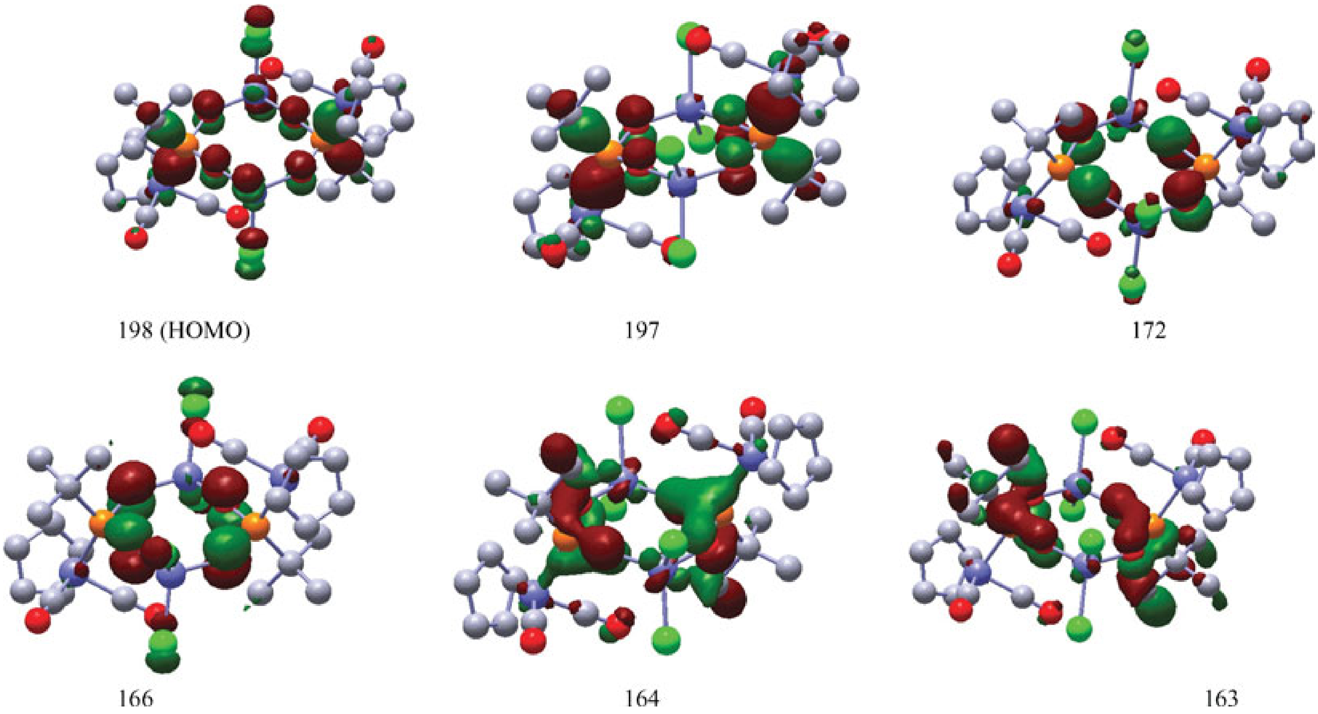

198 (HOMO)
197
172
166
164
163

FIGURE 7 π-Type molecular orbitals of **2** (see Table 3).

Yield: 33 mg (33%). EI-MS (^{m}NBA): $m/z = 791$ $[M{-}2CO]^+$, 692, 664 $[M{-}2CO{-}2Cl{-}nCO]^+$ ($n = 0, 2$). IR (KBr): $\nu(PO_2) = 971$, 1070 cm^{-1}, $\nu(CO) = 1999$, 2044 cm^{-1}. $C_{22}H_{28}Cl_4Fe_4O_8P_2 \cdot 2CH_3CN$ (929.7): calc. C 33.6, H 3.7, Cl 15.1. Found C 33.1, H 3.9, Cl 14.3.

Magnetic Measurement of **2**

Magnetic measurements have been carried out with a SQUID MPMS XL (Fa. Quantum Design) at 200–300 K and a field strength up to 5.5 T. A magnetic moment of $\mu = 6.04\ \mu_B$ and a Curie temperature $\Theta = -58.44$ K were obtained after diamagnetic correction (uncorrected values: $\mu = 6.14\ \mu_B$, $\Theta = -61.37$ K). Cooperative effects (such as ferromagnetism) between two iron centers can be excluded due to the linear dependency between the measured magnetic moment and the magnetic field at 4.2 K. It is assumed that the fairly large distance (4.576 Å) between the two Fe^{3+}–Fe^{3+} centers prevents such interactions.

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