Published in final edited form as:

Inorg Chem. 2008 December 15; 47(24): 11734–11737. doi:10.1021/ic801459s.

A Mixed-Valence Octanuclear Iron-Oxo Pyrazolate: Assessment of Electronic Delocalization by Structural and Spectroscopic Analysis

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Abstract

A formally Fe^{III}₇Fe^{II} complex, containing an inner Fe₄O₄-cubane and four peripheral Fe-centers, is derived from the one-electron reduction of its Fe^{III}₈ precursor. Spectroscopic analysis of the former reveals that the redox activity of this Fe₈-system is confined within its cubane core. The resulting (Fe₄O₄)³⁺-cubane, which is valence-delocalized in the NMR, Mössbauer and IR, but valence-trapped in the X-ray photoelectron spectroscopy (XPS) timescale, is better described as a Robin-Day class-II system by the analysis of its near infrared (NIR) intervalence charge transfer (IVCT) band profile.

Introduction

Intramolecular electron transfer processes associated with mixed-valence complexes are of fundamental importance in chemistry, physics as well as in biology.¹ In-depth pioneering work on *dinuclear* charge transfer complexes by Taube, followed by seminal contributions by others, has established the theoretical basis for understanding these complexes and associated electron transfer events.² In contrast, the paucity of spectroscopic data on electron transfer phenomena pertaining to *polynuclear* transition metal complexes, as recently pointed out also by Keene and co-workers,³ remains a challenge. The Fe-S proteins found in Nature containing redox active Fe₄S₄ cubanes are essential components in biological electron transfer processes, e.g. photosynthesis, cell respiration, nitrogen fixation, and as catalytic sites in hydrogenases.⁴ While no analogous Fe₄O₄ cubane has been unequivocally characterized in a metalloprotein, the possibility of such a future discovery has been suggested.⁵⁻⁷

Earlier, the syntheses of a series of neutral all-Fe^{III} complexes, [Fe₈(μ₄-O)₄(4-R-pz)₁₂X₄], where pz = pyrazolato anion, X = Cl, R = H (**1**), Cl (**2**), Me (**3**) and X = Br, R = H (**4**), were reported by us, along with the full spectroscopic, theoretical and magnetic study of **1**.⁵ These complexes can be electrochemically reduced in four consecutive steps from the

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homovalent $[\text{Fe}_8]$ to the mixed valent $[\text{Fe}_8]^{4-}$.⁵ The octanuclear complexes **1** – **4** contain two types of Fe^{III} -sites, six-coordinate cubane-Fe (Fe_{c}) and five-coordinate outer-Fe (Fe_{o}), either one, or both, of which can be the site of redox activity (Scheme 1). The present work focuses on the structural and spectroscopic characterization of the $[\text{Fe}_8]^-$ species **2**[−] in an effort to identify the site of redox activity and probe the issue of charge localization/delocalization in the mixed valence complex. Two more Fe^{III} -complexes containing $\text{Fe}_8(\mu_4\text{-O})_4$ -cores similar to those of **1** – **4** are known, but their redox activity has not been reported.^{8,9}

Results and Discussion

The reaction of **2** with one equivalent of $^n\text{Bu}_4\text{NBH}_4$ in CH_2Cl_2 yields the corresponding monoanion **2**[−], isolated in crystalline form as $[\text{Bu}_4\text{N}^+][\text{2}^-]$, after slow evaporation of the mother liquor.⁷ The X-ray crystal structure of $[\text{Bu}_4\text{N}^+][\text{2}^-]$ is shown in Figure 1. Anionic **2**[−] crystallizes in an orthorhombic lattice with a crystallographic two-fold axis running through the centers of two opposite $(\text{Fe}_{\text{c}})_2\text{O}_2$ cubane faces and one-half anion per asymmetric unit. The overall symmetry of **2** (*T* point group) is preserved in the structure of **2**[−] with only statistically insignificant differences between corresponding bond lengths and angles (Table 1).^{5a} This observation is consistent with charge delocalization within the Fe_8O_4 -core. Crystallographic disorder could mask charge localization, albeit this interpretation is inconsistent with the spectroscopic evidence presented here (*vide infra*).

The solution ^1H -NMR spectrum of **2**[−] reveals only one set of paramagnetically shifted resonances for the pyrazole H-atoms, suggesting magnetic equivalence of all twelve pyrazolate rings. The most notable feature of the solid state IR spectrum is the occurrence of a single $\nu(\text{Fe-O})$ stretch, observed at 487 cm^{-1} for $[\text{Bu}_4\text{N}^+][\text{2}^-]$, representing a 12 cm^{-1} shift to higher energy compared to that of **2**.^{5a} Both NMR and IR results are consistent with charge delocalization at the respective timescales.

The Fe-2p XPS spectra of solid **2** and $[\text{Bu}_4\text{N}^+][\text{2}^-]$ are shown in Figure 2. For **2**, deconvolution of the Fe-2p_{3/2} and Fe-2p_{1/2} peaks, each into two components, identifies the equal contributions of the five-coordinate outer- Fe^{III} atoms (711 and 725 eV) and six-coordinate cubane- Fe^{III} atoms (713 and 727 eV). Significantly, the deconvolution of the spectrum of $[\text{Bu}_4\text{N}^+][\text{2}^-]$ requires the inclusion of the above two Fe^{III} components, now with unequal contributions, as well as that of a third component at 709 and 723 eV, the latter assigned to a cubane- Fe^{II} center. The decrease of intensity of only one of the two sets of XPS peaks indicates that the one-electron reduction is limited to one of the two sites. Mössbauer spectroscopy (*vide infra*) identifies the Fe_4O_4 cubane as the reduction site. The identification of distinct cubane- Fe^{III} and cubane- Fe^{II} sites in **2**[−] indicates charge localization at the XPS timescale (10^{-17} s).

The Mössbauer spectra of **2** and **2**[−] at 78 K (Figure 3) comprise three lines, the latter showing a characteristic shift of the highest energy line of $\sim 0.14\text{ mms}^{-1}$ toward higher values, indicative of an overall increase of both isomer shift (δ) and quadrupole splitting (E_{Q}) parameters, as expected for a one-electron reduction of **2**. Moreover, a doublet accounting for 1/8 of total iron attributable to a high spin Fe^{II} site is clearly absent in the

spectrum of 2^- , excluding the possibility that the one-electron reduction is localized on a specific iron site. Spectra of 2^- recorded in the 4.2 – 300 K range exhibit little variation (apart from a second order Doppler effect-dependent shift), suggesting that delocalization persists over the entire temperature range at the Mössbauer timescale.

The simulation of 2^- assumes two nested doublets in agreement with the earlier interpretation of the Mössbauer spectrum of **1.5a**. Two crossed quadruple doublets are used for 2^- , showing that the one-electron reduction leaves the outer Fe-sites unaffected, while both δ and E_Q increase substantially (Table 2). The average increase of 0.14 mms^{-1} of the isomer shift of the four cubane-Fe sites upon one electron reduction is equivalent to an increase of $4 \times 0.14 = 0.56 \text{ mms}^{-1}$ for a single Fe-atom, which is the expected increase for a high spin Fe^{III} to a high spin Fe^{II} transition.¹⁰ An alternative simulation of the spectrum of 2^- using a two nested doublet model (**SI**) suggests delocalization over both types of Fe-sites, inconsistent with the XPS spectroscopic results, which show that reduction is restricted to one of the two Fe-sites.

A UV-vis-NIR spectrum was recorded for $[\text{nBu}_4\text{N}^+](2^-)$ in CH_2Cl_2 solution at 298 K. In the UV-Vis region, the LMCT band manifolds of **2** shifts to lower energy in the spectrum of 2^- (**SI**). In the NIR region (Figure 4), a new weak band at $\nu_{\text{max}} = 6270 \text{ cm}^{-1}$ ($\epsilon = 2500 \text{ mol}^{-1} \text{ cm}^{-1}$, $\nu_{1/2} = 3330 \text{ cm}^{-1}$) for 2^- was observed and assigned to an IVCT transition, excluding the possibility of a valence-trapped situation (*localization*).^{2b} The spectrum of 2^- was also recorded in CH_3CN , THF, and $(\text{CH}_3)_2\text{CO}$ with no observable effect on position and intensity of the IVCT band. The occurrence of the IVCT band in an otherwise clear region of the spectrum allows its analysis on the basis of classical two-state theory.^{2b} The theoretical foundation for such analyses has been based on studies of dinuclear Creutz-Taube type systems, but is equally applicable to polynuclear ones.³ The experimental bandwidth at half-height, $\nu_{1/2}$, is narrower than the corresponding theoretical one, $\nu_{1/2}^0$, given by $\nu_{1/2}^0/\text{cm}^{-1} = [16RT\ln(2)\nu_{\text{max}}]^{1/2} = 3777 \text{ cm}^{-1}$, where $16RT\ln(2) = 2310 \text{ cm}^{-1}$ at 298 K. Subsequently, the empirical parameter $\Gamma = 1 - (\nu_{1/2})/(\nu_{1/2}^0)$ takes the value $\Gamma = 0.12$, classifying this species as a Robin-Day type-II system ($0 < \Gamma < 0.5$), or a weakly coupled delocalized system. The electronic coupling factor H_{ab} is estimated by $H_{\text{ab}} = 2.06 \times 10^{-2} (\nu_{\text{max}} \epsilon_{\text{max}} \nu_{1/2})^{1/2} / r_{\text{ab}}$, taking the value $H_{\text{ab}} = 1540 \text{ cm}^{-1}$.¹¹ The above value, calculated here using the average of the crystallographically determined Fe – Fe distances within the mixed-valent Fe_4O_4 cubane, $r_{\text{ab}} = 3.061 \text{ \AA}$, represent only the lower H_{ab} limit.^{2d}

Scheme 2 shows a potential energy versus nuclear configuration plot for a Robin-Day type-II system, like 2^- . The energy of optical electron transfer, E_{op} , is equal to the reorganization energy, $\lambda = 6270 \text{ cm}^{-1}$ for 2^- . The reorganization energy is further analyzed into inner (λ_i , internal structural reorganization) and outer (λ_o , solvent reorganization) components, $\lambda = \lambda_i + \lambda_o$. Because of the solvent-independent behavior of the IVCT band of 2^- , we estimate that λ_o is a minor contributor to λ and $\lambda_i \approx 6000 \text{ cm}^{-1}$. E_{th} is the thermal energy barrier, between the degenerate states. Because the electronic coupling, H_{ab} , is smaller than $\lambda/2$, the lower surface energy consists of double minima. For such systems the thermal electron transfer barrier, E_{th} , is given by $E_{\text{th}} = (\lambda/4) - H_{\text{ab}}$, taking the value of $E_{\text{th}} = 28 \text{ cm}^{-1}$ for 2^- .^{2c}

In summary, the spectroscopic data presented here confine the value of electron-transfer rate among the Fe-centers of the mixed valent Fe_4O_4 -cubane of 2^- between the timescale limits of those probes that identify the charge as delocalized - X-ray crystallography, ^1H -NMR (s), Mössbauer and IR spectroscopy (10^{-8} s, slow limit) - and the timescale of XPS (10^{-17} s, fast limit), which identifies it as localized. The timescale of electronic spectroscopy ($\sim 10^{-15}$ s), which classifies 2^- as weakly coupled system, is our current best estimate of the electron-transfer rate. Examples of other delocalized systems exhibiting valence localization of the ground state at the XPS time scale exist in the literature.¹² The present study provides an entry to the spectroscopic investigation of oxo-analogues of the well studied and biologically relevant Fe_4S_4 -cubanes.⁴ The spectroscopic data of $(\text{Fe}_4\text{O}_4)^{4+}$ and $(\text{Fe}_4\text{O}_4)^{3+}$ may assist the recognition of the Fe_4O_4 -cubane motif in an electron-transfer protein, if such proteins indeed exist.^{5,7} Detailed spectroscopic, magnetic, kinetic and theoretical studies of the above species, as well as of their corresponding $(\text{Fe}_4\text{O}_4)^{2+/-/0}$ redox-modified derivatives, are currently in progress.

Experimental Section

FeCl_3 , pyrazole and tetrabutyl ammonium chloride ($^n\text{Bu}_4\text{NBH}_4$) were obtained from commercial sources and used as received. 4-Cl-pyrazole as prepared by a literature procedure.¹³ Anhydrous CH_2Cl_2 (99.8%) was obtained from commercial source and any other solvent was taken from MBraun solvent Purification system.

Synthesis of $[^n\text{Bu}_4\text{N}^+][2^-]$

$^n\text{Bu}_4\text{NBH}_4$ (7.7 mg, 0.030 mmol) was added to a CH_2Cl_2 (anhydrous, 15mL) solution of **2** (50 mg, 0.027 mmol) under N_2 , resulting in an immediate color change from reddish orange to yellowish brown. The solution was stirred for 2 h, filtered and the filtrate was taken to dryness under reduced pressure to obtain a brown solid, which was dried under vacuum over CaCl_2 overnight. The dry solid was washed with anhydrous MeOH (47 mg, 84%) and stored under N_2 . X-ray quality crystals were grown by slow evaporation of a $[^n\text{Bu}_4\text{N}^+][2^-]/\text{CH}_2\text{Cl}_2$ solution. ^1H -NMR (CDCl_3 , ppm): 14.93 (H^3 , s, $w_{1/2} = 102$ Hz), 7.65 (H^5 , s, $w_{1/2} = 66$ Hz), 108-3.15 (^nBu). UV-vis-NIR (CH_2Cl_2 , cm^{-1}): 28330 ($\epsilon = 80000 \text{ mol}^{-1} \text{ cm}^{-1}$), 22000 (shoulder), 6270 ($\epsilon = 2500 \text{ mol}^{-1} \text{ cm}^{-1}$). IR (KBr pellet, cm^{-1}): 486 (s), 571 (vw), 614 (w), 2760 (m), 959 (w), 1043 (s), 1143 (w), 1170 (m), 1268 (s), 1365 (s), 1417 (m), 1490 (m), 2871 (w), 2932 (w), 2961 (w).

Physical measurements

The electronic spectra of the complexes in solution were recorded on a Varian CARY 500 scan instrument in 200-3200 nm range. Infrared spectra (KBr pellets) were recorded on Nicolet 750 FTIR spectrophotometer. ^1H NMR data were recorded on a Bruker AVANCE DPX-300 spectrometer. Mössbauer spectra were recorded with powdered samples with constant-acceleration conventional spectrometer with a source of ^{57}Co (Rh matrix). Spectra in the 4.2-300K temperature range were obtained using an Oxford cryostat. Isomer shift values (δ) are reported relative to iron foil at 293K. XPS measurements were carried out with a PHI 5600 ESCA system (Physical Electronics). The spectra were analyzed by using the program WMOSS (Web Research, Edina, MN).

X-ray Crystallographic Data Collection and Refinement of the Structure

X-ray diffraction data for $[\text{nBu}_4\text{N}^+][2^-]$ was collected from single crystal mounted atop glass fibers with a Siemens SMART 1K CCD diffractometer, 14a was corrected for Lorentz and polarization effects. 14b The structure was solved employing the *SHELX-90* 14c program and refined by least-squares methods on F^2 , via *SHELXTL-93* 14d, incorporated in *SHELXTL, version 5.1*. 14e Crystallographic details for $[\text{nBu}_4\text{N}^+][2^-]$ are summarized in Table 3.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Financial support from NIH SCoRE S06GM008102 is acknowledged.

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Figure 1.
X-ray crystal structure of $[\text{nBu}_4\text{N}^+][2^-]$; Fe-gold, O-red, N-blue, Cl-green.

Figure 2.

XPS spectra in the Fe-2p region of **2** (top) and $[\text{nBu}_4\text{N}^+][\mathbf{2}^-]$ (bottom). Outer- Fe^{III} , blue trace; cubane- Fe^{III} , green trace; cubane- Fe^{II} , pink trace. The feature at 719 eV is a satellite of the main $2p_{3/2}$ peak.

Figure 3.

^{57}Fe -Mössbauer spectra of powder samples of **2** and $[\text{nBu}_4\text{N}^+][\text{2}^-]$ at 78 K. Solid lines are simulations assuming two nested doublets for **2** and two crossed doublets for **2⁻**. Blue, cubane-Fe; red, outer Fe.

Figure 4.
NIR spectra of **2** and **2⁻** (red) in CH₂Cl₂, 298 K.

Scheme 1.

Scheme 2.

Table 1Selected Bond Distances (Å) and Interatomic Angles (°) for **2**, and **2[−]**.

	2^a	2[−]
Fe _c – O	2.047(2)	2.039(2)-2.050(2)
Fe _c – N	2.101(3)	2.086(3)-2.103(3)
Fe _c ...Fe _c	3.073(2)	3.061(2)-3.064(2)
Fe _c – O – Fe _c	97.3(2)	96.05 (10)-97.32(10)
O – Fe _c – O	82.2(2)	82.19(9)-83.43(10)
Fe _o – O	1.930(4)	1.919(2), 1.931(2)
Fe _o – Cl	2.293(2)	2.279(1), 2.299(1)
Fe _o – N	2.028(3)	2.012(3)-2.043(3)
O – Fe _o – Cl	180.0(1)	178.71(9), 178.73(8)
N – Fe _o – N	119.6(1)	118.45(13)-120.81(14)
Fe _o ...Fe _o	5.843(2)	5.849(2)-5.885(2)
Fe _o ...Fe _c ^b	3.4432(8)	3.441(2), 3.448(2)
Fe _o ...Fe _c ^b	5.460(1)	5.450(2)-5.457(2)

^aReference 5a.^bThere are three short and one long Fe_o...Fe_c distances per Fe-atom, between the vertexes of co-central tetrahedra formed by the four Fe_c and four Fe_o atoms, respectively.

Table 2

^{57}Fe -Mössbauer parameters of **2** and $[\text{nBu}_4\text{N}^+][\text{2}^-]$ at 78 K.

	Fe site	δ (mm/s)	E_Q (mm/s)
2	Cubane	0.45(1)	0.26(2)
	Outer	0.34(1)	0.70(2)
$[\text{nBu}_4\text{N}^+][\text{2}^-]$	Cubane	0.59(1)	0.56(2)
	Outer	0.35(1)	0.73(2)

Table 3Crystallographic Data for $[\text{nBu}_4\text{N}^+][2^-]$

formula	$\text{C}_{52}\text{H}_{60}\text{N}_{25}\text{Cl}_{16}\text{O}_4\text{Fe}_8$
crystal size, mm^3	$0.15 \times 0.14 \times 0.07$
f_w	2113.25
space group	<i>Pbcn</i>
a , Å	18.078(4)
b , Å	26.212(5)
c , Å	18.023(4)
V , Å ³	8540(3)
Z	4
ρ_{calcd} , Mg cm^{-3}	1.644
$2\theta_{\text{max}}$, deg	56.54
μ (Mo K α), mm^{-1}	1.875
reflns collected	53521
unique reflns/ $I > 2\sigma(I)$	9905/4353
no. of params/restraints	476/5
R_1^a/GOF^b	0.0399/0.863
$wR_2^c(I > 2\sigma(I))$	0.0883

$$^a I > 2\sigma(I). R_1 = \sum ||F_o| - |F_c| | / \sum |F_o|.$$

$$^b \text{GOF} = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}.$$

$$^c wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}, \text{ where } w = 1/\sigma^2(F_o^2) + (aP)^2 + bP, P = (F_o^2 + 2F_c^2)/3$$