as the oxidant. The O_2 reaction was at O_2 saturation while the H_2O_2 concentration was made 0.49 M. The HO(DMPO)• signals that were obtained with Fe^{II}(HAPH) and H_2O_2 are seen in Figure 7A and those with O_2 in Figure 7B. When the amplitudes of the second- or third-derivative lines of HO(DMPO)• are compared and scaled for differences in receiver gain settings, molar amounts of Fe^{II} present, and the 3e required to form one HO• from O_2 vs 1e per HO• from H_2O_2, it is observed that Fe^{II}(HAPH) is 53% as efficient as Fe^{II}(BLM) in HO• generation via O_2. The H_2O_2 oxidation of Fe^{II}(HAPH) is 63% as efficient as the Fe^{II}(BLM)/O_2 system. The absolute magnitudes of these numbers may vary slightly with O_2 flow rate and the total initial Fe^{II} concentrations because the species being trapped are reducible by Fe^{II} competitively. However, under very similar initial Fe^{II} concentrations and virtually identical procedures of mixing, these results show that Fe^{II}(HAPH) has a reactivity with O_2 very comparable to that of Fe^{II}(BLM).

Conclusions. Both the Fe^{II}(HAPH) and Cu^{II}(HAPH) complexes behave similarly to their Fe^{II}(BLM) and Cu^{II}(BLM) counterparts. Very similar ESR and electronic spectra have been found for Fe^{II} and Cu^{II} HAPH complexes compared to the BLM, PYML, and AMPHIS chelates and Kimura's "L_2" ligand.[47] The pH = 7 form of Fe^{II}(HAPH) appears to be the same as one of the N_4 isomers for Cu^{II}, but the additional evidence of a protonated imidazole with $pK_a \approx 7.8$ is suggested from an equilibrium shift with HPO_4^{2-} present and by a slight break in the potentiometric titration curve of Fe^{II}(HAPH). The cyclic voltammetry clearly shows axial coordination at pH $\geq$ 8.5 for Fe^{II}(HAPH).

Synthesis of the HAPH ligand and its Fe^{II}(HAPH) complex provides a hybrid molecule between the BLM core donors and those of the heme and cytochrome metalloproteins[2a] which have an axial imidazole (histidine) donor. Like the Fe^{II} hemes, Fe^{II}(HAPH) binds CO. The Fe^{II}(HAPH) complex also reacts with O_2. It forms O_2^-, reduced to HO• in yields of 53% of that for Fe^{II}(BLM) under spin-trapping conditions. Both Fe^{II}(HAPH) and Fe^{II}(BLM) form CO complexes with comparable stabilities ($K_f \approx 5.4 \times 10^3$ M^{-1}). This translates into a favorable free energy of back-donation of nearly 5.1 kcal/mol from the Fe^{II} center to CO. This is substantially less than the ~38.2 kcal/mol energy of back-donation of $(NH_3)_5Ru^{2+}$ toward CO.[26-28] The electrochemical data reveal a net 9.6 kcal favorability of the Fe^{II} state in the presence of CO (compared to axial H_2O). Assuming the CO complex is low spin, as the Fe^{II}(BLM)CO complex, and assuming the conversion high-spin Fe^{II} to low-spin Fe^{II} costs about 5.5 kcal/mol as estimated from stabilities of Fe^{II}(HS) imidazole vs those of Fe^{II}(LS) imidazole complexes,[43] there should be a net free energy released for binding CO of ~4.1 kcal/mol. This is in excellent agreement with the 5.1 kcal/mol estimated from the K_{CO} constant for formation of Fe(HAPH)CO^+. The significant reactivity of the Fe^{II}(HAPH)/O_2 reaction has prompted further work in this laboratory to synthesize molecules containing the HAPH chelation moiety and related units for the purpose of antitumor drug design.

Acknowledgment. We gratefully acknowledge support under NSF Grant CHE-8417751 and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank A. Marcus and J. F. Siuda for assistance in obtaining the HRMS data.

Supplementary Material Available: Visible spectra of the complexes Cu^{II}(HAPH) and Cu^{II}(BLM) (Figure SM-1), Fe^{II}(SAPH-3) and Fe^{II}(SAPH-3)CO (Figure SM-2), and Fe^{II}(BLM) and Fe^{II}(BLM)CO (Figure SM-3) and the FTIR spectrum of $[Cu(HAPH)](ClO_4)\cdot 1.61H_2O$ (Figure SM-4) (4 pages). Ordering information is given on any current masthead page.

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Binding of Fluoride to Copper Zinc Superoxide Dismutase

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Received August 11, 1988

The interaction of fluoride with copper zinc superoxide dismutase (SOD) has been reinvestigated by using both bovine and yeast isoenzymes. The affinity of anions for the latter isoenzyme is larger, and this avoids much of the ionic strength effects connected with weak binding ligands. ^{19}F NMR studies on fluoride in presence of yeast SOD confirm that the anion binds the copper ion. ^1H NMR studies of the Cu_2Co_2SOD derivatives in the presence of F^- indicate that no ligand is removed from coordination. Water ^1H NMR T_1^{-1} measurements on solutions of Cu_2Zn_2SOD–fluoride indicate that exchangeable protons that feel the paramagnetic center are present. This unique behavior of fluoride has opened new perspectives on the understanding of anion binding to copper zinc SOD.

Introduction

The investigation of the binding of anions with copper zinc superoxide dismutase (SOD hereafter) has been a major field of interest[1-4] in the characterization of the enzyme because it can provide information on the catalytic mechanism, as superoxide itself is an anion.

Cyanide and azide were found to be competitive inhibitors[5] whereas cyanate and thiocyanate do not inhibit the enzyme.[6] The ionic strength has some effects on this fast reaction.[7] The binding at the copper ion of CN^-, N_3^-, NCO^-, and NCS^- has been shown by EPR, the spectrum of the enzyme being rhombic and the spectra of the adducts being essentially axial.[1-4] Sometimes the appearance of a charge-transfer band in the electronic spectra is also observed.[8] We have investigated SOD and its derivatives through ^1H NMR spectroscopy on the cobalt-substituted derivative (Cu_2Co_2SOD).[9] The magnetic coupling between copper and cobalt[10] makes the system suitable for ^1H NMR investigation. All the proton signals of the histidines bound to both cobalt and copper are observed well shifted outside the diamagnetic region.

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Table I. ^{1}H NMR Parameters for Cu_2Co_2YSOD and Its Fluoride Adduct at 303 K

signal	proton[a]		shift, ppm (T_1, ms) Cu_2Co_2-YSOD[b]	Cu_2Co_2-YSOD + F^-[b]
A	His-63	Hδ2	65.4 (1.3)	67.5 (<1)
B	His-120	Hδ1	56.6 (5.5)	56.3
C	His-46	Hε2	46.2 (2.5)	47.1 (1.7)
D	His-80	Hδ2	48.5 (3.0)	48.7 (2.0)
E	His-71	Hδ2	48.5 (3.0)	48.7 (2.0)
F	His-80	Hε2	46.2 (2.5)	47.1 (1.7)
G	His-46	Hδ2	40.6 (2.0)	40.4 (1.6)
H	His-120	Hε1	40.6 (2.0)	40.4 (1.6)
I	Asp-81	Hβ1	37.2 (1.2)	36.9
J′	Asp-81	Hβ2	34.1	34.6 (1.5)
J	His-71	Hε2	34.1	34.6 (1.5)
K	His-48	Hδ1	34.1 (5.3)	32.0 (8.3)
L	His-48	Hδ2	27.9 (3.9)	25.8 (4.2)
M	His-46	Hε2	23.9 (2.5)	24.7 (2.2)
N	His-120	Hδ2	24.9 (2.4)	24.6 (2.2)
O	His-48	Hε1	19.5 (2.5)	18.2 (2.5)
P	His-46	Hβ1	17.4 (1.0)	16.5 (2.2)
Q, R	His-46	Hβ2	5.7 (2.9)	−6.5 (3.0)

[a] Assignment from ref 13 and 16. [b] Measured at 300 MHz.

When CN^-[11] or N_3^-[12] are bound to copper, the NMR signals of a histidine, which is bound to copper in the noninhibited system, fall in the diamagnetic (cyanide) or quasi-diamagnetic (azide) region of the spectrum, indicating that this histidine is removed from coordination upon anion binding. Further studies have lead us to assign His-46 (bovine enzyme) as the removed histidine.[13] It is possible that NCO^- and NCS^- behave somewhat in the same way although the final shifts of His-46 protons show that some residual binding remains.[9]

Fluoride has been reported by ^{19}F NMR studies to bind copper in SOD.[14,15] It would be surprising if it were able to detach a histidine ligand. Therefore we thought to reinvestigate this system through ^{1}H NMR spectroscopy of the Cu_2Co_2SOD derivative. However, the affinity of F^- for human and bovine SOD's is on the order of 2 M^{-1};[14,15] and therefore ionic strength effects are strong and may add to the effects of the binding, interfering with our conclusions. We had noticed before that yeast SOD has a larger affinity for anions.[16] Therefore we have investigated through ^{1}H NMR spectroscopy both yeast (Y) and bovine (B) Cu_2Co_2SOD in presence of fluoride. For the native systems also the electronic spectra have been recorded as well as the water ^{1}H T_1^{-1} values at various magnetic fields. In this way we are going to show that fluoride binds to copper without displacing any protein ligand; only the hexogenous ligand water may be substituted by the anion. A suggestive unifying picture for anion binding is proposed.

Experimental Section

Bovine liver SOD was purchased from Diagnostic Data Inc., Mountain View, CA, whereas yeast SOD was a generous gift of Pharmacia, Uppsala, Sweden. Demetalation of both the isoenzymes was obtained as previously described[9,17] through dyalisis against 0.05 M acetate buffer containing 0.01 M EDTA at pH 3.8 and subsequent exhaustive dialysis against high ionic strength buffer in order to remove bound EDTA. The Cu_2Co_2SOD derivatives were prepared by infusing 2 equiv of Co^{2+} into the apoproteins in 10 mM acetate buffer at pH 5.5, followed by slow addition of 2 equiv of Cu^{2+} and incubation overnight at 4 °C.

The ^{1}H NMRD experiments were performed by using the field cycling relaxometer home built at the IBM laboratories at Yorktown Heights, NY, as previously described.[18] The ^{1}H NMR spectra were obtained on

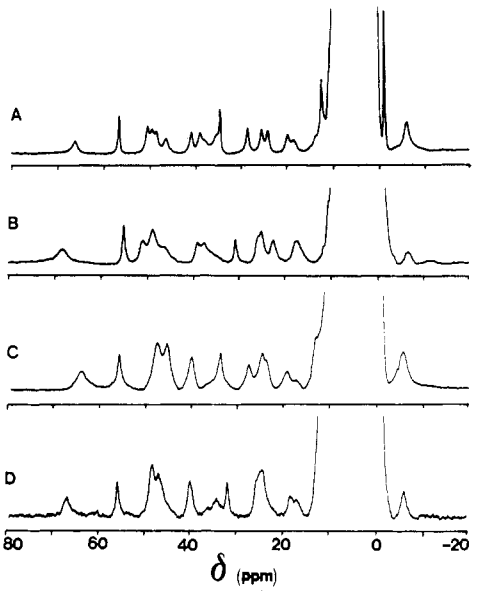

Figure 1. ^{1}H NMR spectra of (A) Cu_2Co_2BSOD in 0.05 M acetate buffer, pH 5.5; (B) Cu_2Co_2BSOD in the presence of 3.5 M F^-; (C) Cu_2Co_2YSOD in acetate buffer, pH 5.5; and (D) Cu_2Co_2YSOD in the presence of 1.4 M F^-. Spectra A and B were recorded at 300 MHz; spectra C and D were recorded at 200 MHz. All the spectra were recorded at 303 K.

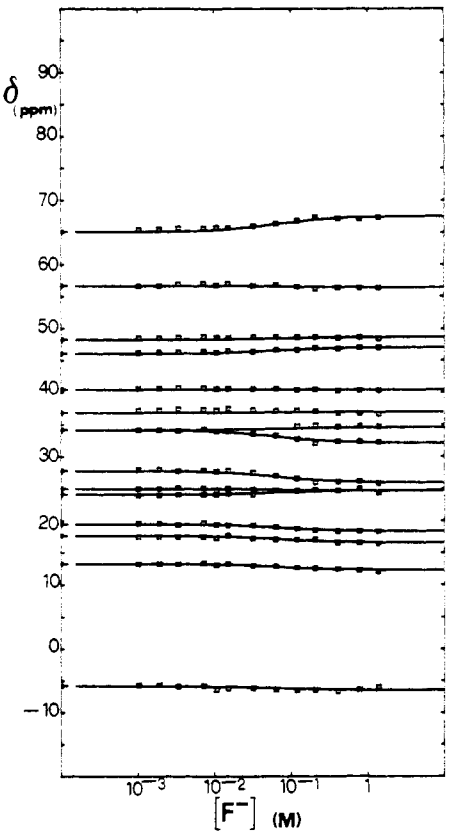

Figure 2. Chemical shift dependence of ^{1}H NMR signals of Cu_2Co_2YSOD in 0.05 M acetate buffer, pH 5.5, on fluoride concentration at 303 K and 200 MHz.

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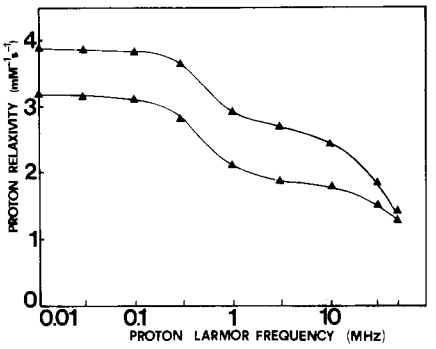

Figure 3. 298 K water proton NMRD profiles of Cu_2Zn_2BSOD in 0.05 M acetate buffer, pH 5.5, in the presence of 3.5 M F^-. For comparison purposes the data for the native enzyme are also reported (lower curve).

a Bruker MSL 200 spectrometer by using the modified DEFT[19,20] pulse sequence in order to suppress H_2O and bulk protein signals. Proton spin–lattice relaxation times were determined on Bruker CXP 300 spectrometer by the modified DEFT sequence by varying the delay time between subsequent pulses, and the values were determined by a nonlinear least-squares fitting of the intensities as a function of the delay time.[20] The 84.7-MHz ^{19}F NMR spectra were recorded on a Bruker CXP 90 spectrometer.

The electronic spectra were recorded on a Cary 17D spectrophotometer; X-band ESR spectra were recorded at room temperature on a Bruker ER 200 spectrometer, and the frequency was calibrated by using DPPH (diphenylpicrylhydrazyl) (g = 2.0036).

Results

^1H NMR Spectra of Cu_2Co_2SOD in the Presence of F^-. In both yeast and bovine enzymes the variations of the shifts of the signals upon addition of increasing amounts of fluoride are very modest, not exceeding 2 ppm for the most affected signal (see Figures 1 and 2 and Table I). The pattern is, however, the same as observed with the other anions, i.e., N_3^-, CN^-, NCO^-, and NCS^-.[9] In particular, signal A moves downfield and signals K and L, which have been assigned to His-48 (yeast) (His-46 for the bovine), move toward the diamagnetic positions. In the case of the yeast enzyme, an affinity constant of 16 ± 8 (3σ) M^{-1} at pH 5.5 can be estimated from the shift dependence on the fluoride concentration of the affected signals A, K, and L, whereas the bovine enzyme shows a very low affinity (titration not shown), which can be estimated as around 2 M^{-1} at the same pH. Such a value is consistent with that previously determined.[14,15] The T_1 values of the resonances have been measured for the adduct of the yeast isoenzyme and are reported in Table I.

^1H NMRD Spectra of Cu_2Zn_2SOD in the Presence of F^-. The water ^1H T_1^{-1} values of 0.44 mM bovine SOD solutions, at pH 5.5, in the presence of increasing fluoride concentrations (up to 3.5 M) have been measured at different fields ranging from 0.23 to 1.17 T, corresponding to 0.01–50-MHz proton Larmor frequencies. The water ^1H T_1^{-1} increases with increasing concentration of fluoride. Again, from the concentration dependence of T_1^{-1} at every magnetic field an affinity constant consistent with the previous data[14,15] is estimated. The measured values at the highest fluoride concentration (3.5 M) have been corrected for the diamagnetic contribution by subtracting the corresponding T_1^{-1} value of the reduced protein and divided by the molar fraction of the bound water giving the fully paramagnetic contribution T_{1M}^{-1} (see Figure 3). T_{1M}^{-1} values provide a quantitative indication of whether there are exchangeable protons feeling a paramagnetic center. In the noninhibited bovine Cu_2Zn_2SOD, a water molecule is present[21] with a copper–oxygen distance of 2.4 Å.[21,22,24] At variance with most of the investigated anions, a slight increase of the T_{1M}^{-1} values with respect to the noninhibited protein is observed.

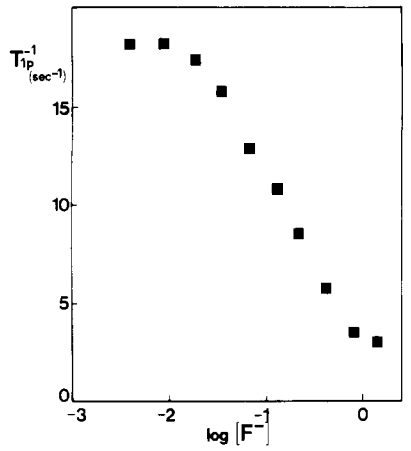

Figure 4. 298 K ^{19}F T_{1p}^{-1} values of 2.1 × 10^{-6} M Cu_2Zn_2YSOD solution in Hepes buffer pH 7.5 as a function of fluoride concentration.

The data of Figure 3 have been treated with a best fitting procedure based on a previously derived equation[22,23] that takes into account the dipolar coupling between the water protons and the S mainfold,[22] whose splitting due to coupling with the magnetic moment of the copper nucleus is also taken into account. The treatment provides an estimate of the correlation time for the magnetic coupling between the water proton and the unpaired electron and a geometrical factor $G = \sum_i 1/r_i^6$ where r is the distance of the ith exchangeable proton from the paramagnetic center. A best fitting procedure of the curves in Figure 3 leads to a G value for the fluoride adduct of 1.3 × 10^{-15} pm^{-6} and a τ_c = 3.1 × 10^{-9} s to be compared with G = 1.2 10^{-15} pm^{-6} and τ_c = 2.4 10^{-9} s for the native enzyme.

Electronic and EPR Spectra. The electronic and EPR spectra of the bovine isoenzyme do not change appreciably in presence or absence of fluoride.[14,15] In the case of the yeast isoenzyme the electronic and CD spectra experience a bathochromic shift upon fluoride binding and an increase in $A_\parallel$ of the EPR spectrum from 143 × 10^{-4} to 158 × 10^{-4} cm^{-1}.

^{19}F T_1^{-1} Measurements. A sample 2.1 × 10^{-6} M of yeast SOD at pH 7.5 was titrated with increasing amounts of a KF solution and the T_1^{-1} value of the ^{19}F NMR signal measured. In Figure 4, the T_{1p}^{-1} values, i.e. the difference between the experimental values and the values of a blank solution containing fluoride at the same pH, corrected for dilution, are reported as a function of F^- concentration. The titration curve can be fitted with an affinity constant of 6 ± 2 (3σ) M^{-1}. This value compares well with the value of 16 ± 8 (3σ) M^{-1} obtained from ^1H NMR spectra in the case of Cu_2Co_2SOD at pH 5.5. The difference in pH may account for the discrepancy. The T_{1p}^{-1} dependence on the F^- concentration indicates that the exchange rate between free and bound fluoride is fast on the NMR time scale. From the estimated value of the affinity constant and taking into account the molar ratio between bound and free fluoride ions an higher limit for T_{1M} of 5 × 10^{-8} s was calculated. This value is very small and is strongly indicative of direct binding to the metal ion. The same conclusions were reached for the bovine isoenzyme.[14,15]

Discussion

Fluoride ion shows a very low affinity toward the bovine enzyme; furthermore, the visible and EPR spectra of the fluoride adduct are extremely similar to those of the native protein, making questionable even the effective binding of this anion.[15] Viglino

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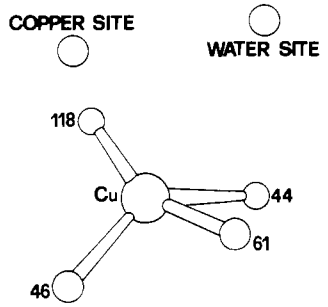

Figure 5. Sketchy representation of the copper chromophore in Cu_2Zn_2SOD showing the bound water and the noncoordinated water molecules arrangment, as proposed by Tainer et al.[28] In their labeling scheme the copper site is the site of the semicoordinated water and the water site is the site of the noncoordinated water.

et al. have shown that ^{19}F relaxation rates of F^- solutions are strongly affected by bovine SOD;[14] furthermore, they were able to prove that the anion binds directly to copper(II) with an affinity constant of about 2 M^{-1}. Whereas the T_{1M}^{-1} values are dominated by the dipolar coupling, the T_2^{-1} values were dominated by τ_m.[14] We feel that measurements at high salt concentrations may give rise to some problems as far as conformational effects on the protein are concerned. For example, the small chemical shift variations observed during the titration with fluoride of the ^1H NMR signals in the Cu_2Co_2BSOD derivative could in principle reflect some minor changes occurring at high ionic strength, rather than being indicative of changes in the metal coordination sphere induced by fluoride binding. For this reason we have extended our investigations to the yeast enzyme, which is known[16] to exhibit a significantly higher affinity for anions than the bovine enzyme. Indeed, from the ^1H NMR data of Cu_2Co_2YSOD as a function of fluoride concentration, an affinity value of 16 M^{-1} is determined, which compares with 2 M^{-1} estimated for the bovine enzyme. Owing to the larger affinity, also the ^{19}F T_1 measurements on the native enzyme can be analyzed with more confidence, a substantial amount of bound enzyme being formed at much lower fluoride concentration. From the affinity constant, the value $(T_{1M} + \tau_m)^{-1} = T_{1p}^{-1}[F]_{tot}/[F]_{bound}$ can be calculated, which is equal to 5×10^{-8} s and represents the higher limit for T_{1M} itself. This value correlates quite well with that calculated by Viglino et al,[14] and again such a short value of T_{1M} demonstrates that fluoride is directly bound to copper.

On the other hand, a close analysis of the shift pattern shown in Figure 2 as well as of the T_1 values of the signals of the histidine protons in the Cu_2Co_2SOD derivative indicates that fluoride produces only minor changes in the copper coordination sphere and no change in the cobalt environment. Indeed, the signals of His-48 (yeast), which correspond to those of His-46 in the bovine enzyme, are only slightly affected by fluoride binding. The T_1 values, which are sensitive to the 6th power of the nucleus–unpaired electron distance, indicate that His-48 in the fluoride adduct remains coordinated to copper without any substantial movement from its original position. In the case of N_3^- and CN^- such histidine does not feel the paramagnetic center.[11,12,26] Some variations are observed for signals P and C–F. Their interpretation is not clear at this stage; we may note that in the case of N_3^-[16] or CN^-[11] the changes in T_1 are in the same direction and are of larger extent.

Proton relaxation dispersion curves of aqueous solutions containing Cu_2Zn_2BSOD indicate that in presence of fluoride there is a small increase in the relaxivity with respect to the native protein, at variance with the behavior of CN^-, N_3^-, and NCO^-.[11] The increase in water proton relaxation rate upon addition of F^- on metalloproteins has already been reported for metmyoglobin.[27] This protein has a water coordinated in slow exchange with the bulk solvent; F^- displaces it and probably binds a water molecule through the H bond, which is now in fast exchange. When fluoride binds copper, it is quite possible that a water molecule is hydrogen bonded to it in such a way that the geometric factor responsible for nuclear relaxation slightly increases. Alternatively, a water molecule may still be semicoordinated. The general features of the fluoride adduct are therefore within the following frames: (a) fluoride is directly coordinated to copper; (b) no histidine may be displaced from coordination; (c) the semicoordinated water molecule may still be present in the adduct. If we refer to the picture proposed by Tainer et al.,[28] the anions could bind at the site where water is bound (Figure 5). If the ligand is weak and/or small like fluoride, it is possible that it binds copper without displacing any other protein ligand. It is also possible that a further water molecule, which is 3 Å above in the structure of the protein, gets closer to copper either hydrogen bonded to fluoride or not. In the case of thiocyanate, the Cu–N (His-48, yeast) bond is weakened more than in the fluoride case but less than in the cyanate and azide cases in that order. The ^1H water relaxivity decreases in the same order. This surprising result may suggest that anions displace His-48 (yeast) to a larger extent the larger the affinity constant. In Figure 6 the limit shifts of the L signal, which in the present assignment monitors His-46 (bovine) (or His 48, yeast), of the ^1H NMR spectra of several anion–Cu_2Co_2SOD adducts, as a function of the affinity constant of the anions, are reported. The curve clearly shows that the chemical shift, that is the sum of the paramagnetic shift and that of the diamagnetic ligand, experienced by this signal, decreases as the affinity constant increases, being almost equal to the diamagnetic value in the case of strong ligands like cyanide. Even for the two isoenzymes the effect of fluoride is larger in the case of larger affinity constant. Finally, we may look at the chromophore as formed by copper(II), N(His-120, yeast numbers), N(His-46), N(His-63, bridging), and the hexogenous anion ligand arranged in a plane, with His-48 in an apical position and possibly water in the other. This last position would correspond to the cleft where a noncoordinated water is present in the native protein.[28] The removal (partial or total) of the ligands in the axial positions would depend on the strength of the hexogenous ligand. The increase in the Cu–N (His-48) distance and the formation of the basal plane could result from both a movement of copper and a small rotation of the histidine.

This picture unifies all the previous suggestions and gives them chemical sense. Lieberman et al. had suggested sizable rotation of the z axis direction upon cyanide binding since now the basal

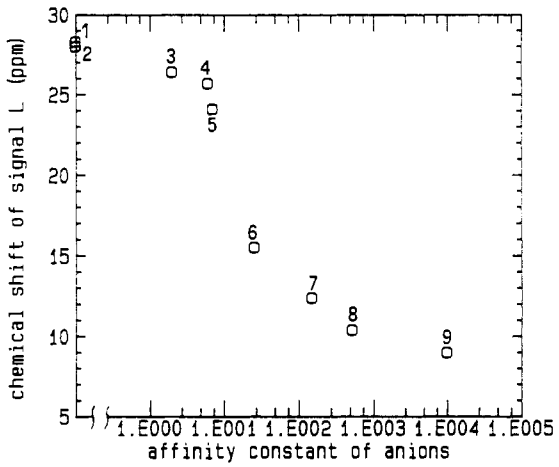

Figure 6. Chemical shift of the L signal (see text) in several anionic adducts of different Cu_2Co_2SOD isoenzymes as a function of the affinity constant of the anion: (3) Cu_2Co_2BSOD–F^-; (4) Cu_2Co_2YSOD–F^-; (5) Cu_2Co_2BSOD–NCS^-; (6) Cu_2Co_2BSOD–NCO^-; (7) Cu_2Co_2BSOD–N_3^-; (8) Cu_2Co_2YSOD–N_3^-; (9) Cu_2Co_2BSOD–CN^-. For this adduct a lower limit of 10^4 for the stability constant has been considered. For comparison purposes also the isotropic shifts in the pure Cu_2Co_2BSOD (1) and Cu_2Co_2YSOD (2) isoenzymes are shown.

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plane is formed by three histidine nitrogens and the anion;[29] Rotilio had suggested that one histidine goes in an apical position upon anion binding;[30] we had suggested that one histidine could be removed from coordination upon anion binding to the enzyme in order to account for the electronic and ^1H NMR spectra of the derivatives.[9,13,15]

Acknowledgment. Thanks are expressed to Dr. S. H. Koenig of the IBM T. J. Watson Research Center, Yorktown Heights, NY, for the use of the NMRD instrument. This work has been performed with the contribution of the CNR, Progetto Speciale "Modelli di Interazione in Macromolecole in Funzione di un loro Utilizzo in Processi Biotecnologici".

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An Unusual Mixed-Metal Cluster: Synthesis and Molecular Structure of $FePt_5(CO)_9(PEt_3)_4$

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Received February 3, 1989

The reaction of $Na_2[Fe(CO)_4]$ with *cis*-$PtCl_2L_2$ (L = PEt_3, PPh_3, P(*p*-Tol)$_3$, PMe_2Ph) in THF yields cluster complexes of nuclearities 3, 5, and 6, and the new hexanuclear heterometallic cluster $FePt_5(\mu\text{-}CO)_4(CO)_5(PEt_3)_4$ (**1**) has been shown by X-ray analysis to possess an unprecedented geometry. The structure of **1** may be regarded as a Pt_4 tetrahedron sharing an edge with a $FePt_3$ lozenge in such a way that the metal core is unusually open (noncompact) for a six-atom cluster. The electron count in this 84-electron cluster is discussed. The structure of **1** shows the topological preference of the iron fragment to bridge a Pt–Pt bond and confirms that deltahedra are energetically the most stable structures, since they possess the greatest connectivities for a fixed number of vertices. Cluster **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.421 (2) Å, b = 23.653 (3) Å, c = 18.877 (3) Å, β = 95.16 (2)°, and Z = 4. The final conventional agreement factors were $R(F_o)$ = 0.058 and $R_w(F_o)$ = 0.062.

Questions of current interest in the rapidly expanding field of molecular cluster chemistry include the identification of optimum geometries of transition-metal clusters and the toposelective design of mixed-metal clusters.[1] It has been recently emphasized that the important bonding effects of the valence d electrons in transition-metal clusters account for the polyhedral structures of the latter being relatively compact, in comparison with the boranes.[2] Here we present a new bimetallic Fe–Pt mixed-metal carbonyl cluster, $FePt_5(\mu\text{-}CO)_4(CO)_5(PEt_3)_4$ (**1**), which has an unprecedented and unusually open structure for a six-atom cluster.

Results

In the course of our studies on the synthesis and catalytic applications of Fe–Pd and Fe–Pt carbonyl clusters,[3] we investigated the reaction of $Na_2[Fe(CO)_4]$ with *cis*-$PtCl_2(PEt_3)_2$ in tetrahydrofuran (THF). Separation of the reaction products by column chromatography afforded among others $Pt_5(\mu\text{-}CO)_5(CO)(PEt_3)_4$[4] and $FePt_5(\mu\text{-}CO)_4(CO)_5(PEt_3)_4$ (**1**) (eq 1, Scheme I). The new cluster **1** was characterized by IR spectroscopy, which indicated the presence of terminal and bridging carbonyl ligands, by $^{31}P\{^1H\}$ NMR spectroscopy, which established that the PEt_3 ligands were all bound to Pt atoms (^1J(PtP) values ranging from 4904 to 3800 Hz), and by fast atom bombardment (FAB) mass spectroscopy, which gave the parent ion and the expected fragmentation patterns (Experimental Section). Brown-red crystals of **1** suitable for X-ray analysis were obtained by slow diffusion of hexane into a chlorobenzene solution at −20 °C. A perspective view of the cluster is presented in Figure 1. A summary of crystal data, intensity collection and structural refinement is given in Table I; selected bond distances and angles are given in Table II, and atom coordinates and isotropic thermal parameters, in Tables III and SII (supplementary material).[16] The metal core geometry may be regarded as a Pt_4 tetrahedron sharing its Pt(1)–Pt(5) edge with a $FePt_3$ lozenge. The latter is created by the triangles FePt(3)Pt(5) and Pt(1)Pt(3)Pt(5), which make a dihedral angle of 2.1° with each other. This lozenge is oriented in such a way that its mean plane is nearly orthogonal to the Pt(1)Pt(2)Pt(4) plane (dihedral

Scheme I

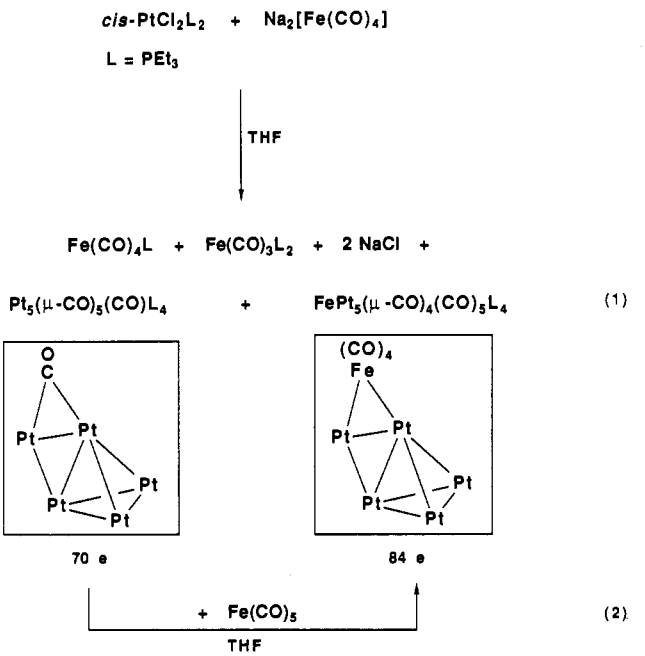

Table I. Crystallographic Data for $FePt_5(CO)_9(PEt_3)_4$

formula: $C_{33}H_{60}FeO_9P_4Pt_5$	fw: 1755.5
a = 11.421 (2) Å	space group: monoclinic $P2_1/n$
b = 23.653 (3) Å	T = 25 °C
c = 18.877 (3) Å	λ = 0.71073 Å
α = 90.00°	ρ_{calcd} = 2.29 g/cm^3
β = 95.16 (2)°	μ = 148 cm^{-1}
γ = 90.00°	$R(F_o)$ = 0.058
V = 5079.0 (6) Å^3	$R_w(F_o)$ = 0.062
Z = 4	

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