reasonable because both ligands have a sulfonate group adjacent to the –OH reaction center of the ligand. The larger value of k_1 for the sulfonate compared to quinizarin indicates that initial complexation is preferred adjacent to the sulfonate group because of more favorable ion pairing in the precursor complex. This also is consistent with the rather similar values of k_2 for these two systems.

The reactivity of the bis(μ-hydroxo)iron(III) dimer is more difficult to categorize because of the few cases where it has been observed. The rate constants for the squarate anion,[28] Tiron,[8] and acetohydroxamic acid[29] are 4.5×10^5, 1.1×10^4, and 8.2×10^3 M^{-1} s^{-1}, respectively. For the systems studied here, the rate constants (k_3 and k_4) are all smaller than these values. It is not clear at present whether this highly variable reactivity reflects an associative mechanism or ligand steric and other structural features. It is noteworthy that the ratio k_3/k_4 is 2 for all the ligands studied here.

The rate constants for daunomycin are substantially smaller than the analogous rate constants for quinizarin or its sulfonate. Dimer formation of daunomycin has not been included in the kinetic analysis of daunomycin. About 50% of the daunomycin is dimerized at our typical concentration of 1×10^{-4} M, so that the rate constants would increase by a factor of ~2 at most if only the monomer was assumed to be reactive. Then, if $k_1 = 2(1.7 \times 10^2)$ for daunomycin it is similar to k_2 for quinizarin-2-sulfonate, and this may reflect the normal reactivity for $FeOH^{2+}$ at a neutral hydroxyquinone site in aqueous solution. The 10 times smaller value of k_2 for daunomycin can be attributed to a steric effect of the aminosugar substituent.

Experimental Section

Materials. Sodium quinizarin-2-sulfonate was prepared by the method of Marshall.[30] The product was recrystallized three times from hot water and charcoal to yield a golden brown-orange solid. The ^1H NMR spectrum (in DMSO at 300 MHz) gave the following chemical shifts (δ in ppm from internal TMS): 7.65 (3 H, singlet), 7.96 (6 and 7 H, seven-line multiplet), 8.25 (5 and 8 H, seven-line multiplet), 12.64 (OH, singlet), 13.28 (OH, singlet). The electronic spectrum in water has maxima at 278, 335, and 462 nm and a shoulder at 486 nm, consistent with the recent report of Mukherjee et al.[27]

Quinizarin (Eastman Chem. Co.) was used as supplied. In the aqueous 42.8% methanol solution used for this work, the electronic spectrum has maxima at 280, 326, and 472 nm, with molar absorptivities of 1.03×10^4, 3.06×10^3, and 7.63×10^3 M^{-1} cm^{-1}, respectively, and a shoulder at ~515 nm.

Daunomycin hydrochloride (daunorubicine) was used as obtained (Sigma Chemical Co). In aqueous 0.01 M $HClO_4$/0.50 M $NaClO_4$ the electronic spectrum has maxima at 288 and 480 nm, with molar absorptivities of 8.02×10^3 and 1.06×10^4 M^{-1} cm^{-1}, respectively, and a shoulder at ~494 nm.

Stock solutions of iron(III) perchlorate in 1.0 M perchloric acid were prepared from iron wire (99.9%, Baker and Adamson) and standarized for iron(III) and H^+ content as described previously.

Equilibrium Measurements. Solutions of ligand and iron(III) at various concentrations and acidities were mixed in volumetric flasks and diluted to volume, and the spectra were recorded between 250 and 700 nm within 2–5 min after mixing. The ligand concentration ranges were $(3.56–4.06) \times 10^{-5}$ M for quinizarin, $(1–2) \times 10^{-4}$ M for quinizarin-2-sulfonate and 1×10^{-4} M for daunomycin. The iron(III) concentrations were in the range 6×10^{-4} to 0.03 M and $[H^+]$ was between 0.01 and 0.06 M. The equilibrium constants were evaluated by least-squares analysis of the variation of absorbance with ligand, iron(III), and H^+ concentrations at 610, 630, and 670 nm.

Stopped-Flow Measurements. Solutions of iron(III) perchlorate at the desired concentration and acidity in 1.00 M $HClO_4/NaClO_4$ were mixed with aqueous solutions of ligand, except that both were in 42.8% methanol for quinizarin. The time–absorbance change (volts) data were collected on a transient recorder. The data was output on a digital voltmeter/printer and then analyzed by least-squares methods to give the model described in the text. Error limits given are 1 standard deviation.

The kinetics were studied between 1.36×10^{-2} and 8.00×10^{-2} M H^+ and 0.436×10^{-2} and 3.49×10^{-2} M iron(III) at ligand concentrations similar to those in the equilibrium study.

Instrumentation. Spectrophotometric measurements were done on a Hewlett-Packard 8451 diode array spectrophotometer equipped with a thermostated cylindrical cell holder.

The stopped-flow studies were done on a Tritech Dynamic Instruments system. The flow system is glass and Teflon, and the reservoir and drive syringes are immersed in a thermostated water bath with the temperature regulated to 25 °C by a YSI thermistor controller.

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Registry No. **1**, 20830-81-3; **3**, 81-64-1; **4**, 114033-82-8; $Fe(H_2O)_6^{3+}$, 15377-81-8.

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Notes

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Kinetic and Thermodynamic Synergism of Chloride and Carbon Monoxide Binding to Bis(acetonitrile)bis((dimethylglyoximato)difluoroborato)iron(II)

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Introduction

Extensive investigations of CO binding to low spin FeN_4L_2 systems involving a tetradentate macrocyclic ligand (N_4) and a variety of neutral axial ligands (L) have been previously described.[1-4] Here we describe some remarkable effects of anions on the CO binding properties of the bis(acetonitrile) complex of bis((dimethylglyoximato)difluoroborato)iron(II) $Fe(dmgBF_2)_2(CH_3CN)_2$ (denoted as FeN_4A_2 hereafter) in acetonitrile solution.

Experimental Section

Materials. The complex FeN_4A_2 was prepared as described previously.[3] Tetraethylammonium cyanide and chloride and tetrabutylammonium thiocyanate and bromide (Aldrich) were used as received. Solvents and other reagents were of the highest purity available. Kinetic results were unaffected by drying the acetonitrile or on addition of small amounts (1%) of water.

Synthesis. **$[Et_4N][FeN_4(CN)(CO)]$.** Solid FeN_4A_2 (120 mg, 0.26 mmol) was added to 50 mL of CO-saturated tetrahydrofuran and stirred during dropwise addition of a CH_2Cl_2 solution of tetraethylammonium cyanide (40 mg). Concentration of the solution with CO purging resulted in a yellow precipitate, which was filtered off and dried in vacuo (yield 70 mg, 62%). IR (KBr): 2030 (ν_{CO}), 2200 (ν_{CN}) cm^{-1}.

Physical Measurements. Visible spectra were recorded using an Aminco DW-2a UV/vis spectrophotometer with temperature maintained at 25 ± 0.1 °C. Fast reactions were monitored using an Applied Photophysics flash photolysis apparatus and data processed as described pre-

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Table I. Spectroscopic and Kinetic Data[a] for FeN_4 Complexes in CH_3CN at 25 °C

X	λ_{max}, nm (log ϵ)		K_X,[b] M^{-1}	k_2, atm^{-1} s^{-1}	K_Xk_2, M^{-1} atm^{-1} s^{-1}	k_{-X}, s^{-1}
	FeN_4AX	FeN_4XCO				
CH_3CN	444 (3.88)	350–370 (3.64)	1	0.025	0.025	1000[c]
Br-		410 (3.48)	0.1[d]	250[d]	25 (5)	15000 (2000)
Cl-	430 (3.36)	405 (3.57)	10 (5)	8 (1)	200 (50)	185 (15)
NCS-	480 (3.74)	393 (3.62)	500 (50)	0.2 (0.01)	100 (20)	2 (0.5)
CN-	494 (3.96)	382 (3.81)	$>10^5$	0.0011		

[a] Standard errors by linear least-squares fits are given in parentheses. [b] Spectrophotometrically determined; experimental errors are given in parentheses. [c] Reference 4. [d] Estimated as described in text.

viously.[3] Infrared spectra were obtained on a Nicolet 20sx FTIR instrument as KBr disks.

Samples of FeN_4XCO^- (X = Cl^-, NCS^-, Br^-) were photolyzed in CO-saturated CH_3CN at 25 °C in 10-cm Pyrex cells ([Fe] = 2×10^{-5} M), and recombination with CO was monitored by the decrease at 444 nm. Rates were shown to be [CO] dependent by purging with nitrogen. A faster process associated with anion dissociation results in an increase at 444 nm. For X = NCS^-, a decrease at 480 nm was also monitored.

Slower kinetic determinations were made by standard spectrophotometric methods in CH_3CN solution in 1-cm pyrex cuvettes with [Fe] typically 2×10^{-4} M as described previously.[2b] Equilibrium constants were obtained from a nonlinear least-squares fit of spectrophotometric titration data covering saturation between 20% and 80%.

Results and Discussion

The binding of anions (eq 1) to the labile FeN_4A_2 were determined spectrophotometrically (Figure 1) by titration with

$$FeN_4A_2 + X^- \overset{K_X}{\rightleftharpoons} FeN_4AX^- + A \qquad (1)$$

tetraalkylammonium salts in CH_3CN affording the data given in Table I. The relative affinity of X^- is in the order CN ≫ NCS > Cl > Br. The anionic derivatives, like other Fe(II) complexes, readily bind CO, giving much more inert complexes with MLCT bands in the 350–400-nm range.[4] The anionic $FeN_4X(CO)^-$ complexes are spectrally distinct from the previously characterized $FeN_4A(CO)$.

Reaction of FeN_4A_2 in CO saturated CH_3CN in the presence of anions proceeds according to eq 2, 3, or 4, depending upon conditions. The dependence of the pseudo-first-order rate constant

$$FeN_4A_2 + CO \rightarrow FeN_4A(CO) + A \qquad (2)$$

$$FeN_4A_2 + CO + X^- \rightarrow FeN_4X(CO)^- + 2A \qquad (3)$$

$$FeN_4AX^- + CO \rightarrow FeN_4X(CO)^- + A \qquad (4)$$

for CO binding on $[X^-]$, shown in Figure 2, fits the equation

$$k_{obs} = (k_1 + K_Xk_2[X^-])/(1 + K_X[X^-]) \qquad (5)$$

where, based on the D mechanism below and approximations appropriate[5a] in neat CH_3CN

$$k_2 = k_{-A}{}^{X}k_{+CO}{}^{X}[CO]/(k_{+A}{}^{X}[A]) \qquad (6)$$

$$k_1 = k_{-A}{}^{A}k_{+CO}{}^{A}[CO]/(k_{+A}{}^{A}[A]) \qquad (7)$$

$$\begin{tikzcd}
FeN_4A_2 \arrow[r, shift left, "k_{-A}{}^{A}"] & FeN_4A \arrow[l, shift left, "k_{+A}{}^{A}"] \arrow[r, shift left, "k_{+X}{}^{A}"] \arrow[d, "k_{+CO}{}^{A}"] & FeN_4AX^- \arrow[l, shift left, "k_{-X}{}^{A}"] \arrow[r, shift left, "k_{-A}{}^{X}"] & FeN_4X^- \arrow[l, shift left, "k_{+A}{}^{X}"] \arrow[d, "k_{+CO}{}^{X}"] \\
& FeN_4ACO & & FeN_4XCO^-
\end{tikzcd} \qquad (8)$$

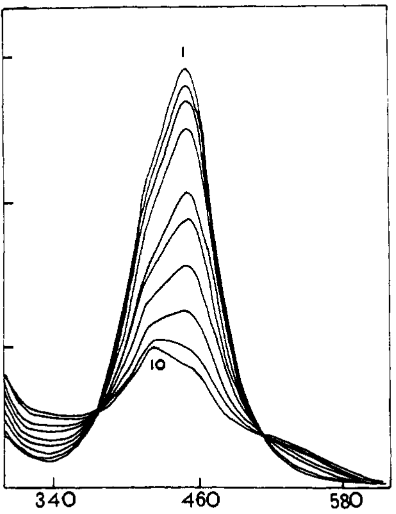

Figure 1. Spectrophotometric data for the titration of FeN_4A_2 with $[Et_4N]Cl$ in CH_3CN at 25 °C. Spectra 1–10 are for $[Cl^-]$ = 0, 3.65, 7.16, 13.8, 66.0, 114, 204, 490, 1120, and 1760 mM, respectively.

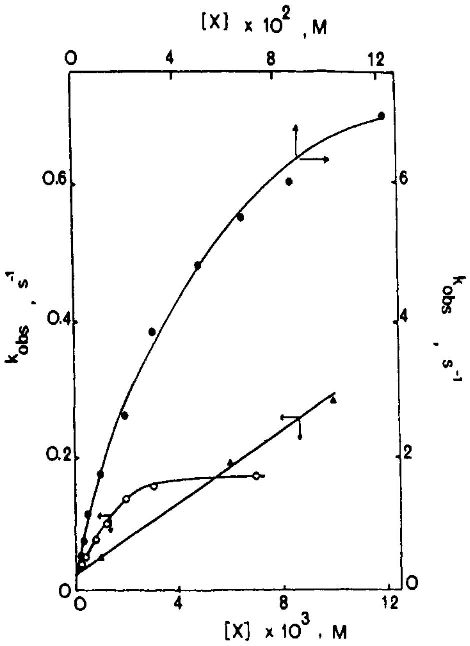

Figure 2. Anion dependence of the rate of CO binding (eqs 2–4) in CO-saturated CH_3CN at 25 °C: (▲) Br-; (○) SCN-; (●) Cl-.

Least-squares fit of the data for Cl^- and NCS^- to a plot of $1/(k_{obs})$ vs 1/[X] gives a value of K_{Cl} = 25 ± 10 M^{-1} and K_{NCS} = 500 ± 50 M^{-1} in good agreement[5b] with the spectrophotometrically derived values in Table I. Values of the limiting rates, k_2, derived

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(5) (a) Equation 5 is derived by assuming rapid equilibrium between FeN_4A_2 and FeN_4AX^-, steady-state conditions for FeN_4A and FeN_4X^-, and $k_{+A}{}^{A} \gg (k_{+X}[X] + k_{+CO}[CO])$. (b) The discrepancy for Cl^- is likely a result of ionic strength effects, a dependence of CO solubility on dissolved salts, and/or a breakdown in the approximation above at high [X].

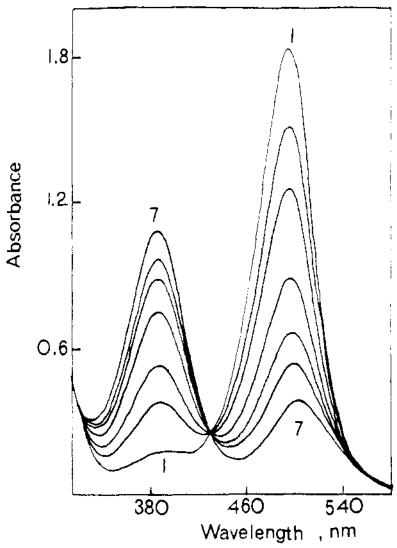

Figure 3. Spectral changes with time for CO binding to $FeN_4A(CN)^-$ in CO-saturated CH_3CN at 25 °C. Spectra 1–7 were recorded at times 0, 5, 10, 15, 25, 36, and 80 min.

from the analysis are also given in Table I. In the case of Br^- no curvature in the plot is observed since K_{Br} is small; however, estimates of k_2 and K_{Br} can be made on the basis of data given below. For CN^-, eq 1 lies all the way to the right and only reaction 4 is observable (Figure 3).

It is important to note in the reaction at low $[Cl^-]$ according to eq 3 that Cl^- binding clearly precedes CO binding since FeN_4ACO does not react with Cl^- on this time scale. The accelerated rate of CO binding in the presence of Cl^- may be described as kinetic synergism. Thermodynamic synergism occurs with respect to the Cl^- ligation since the extent of Cl^- binding is much greater in the presence of CO (eq 3) than in its absence (eq 2).

The origin of this kinetic synergism is easily understood in terms of the well-established dissociative mechanism for ligand substitution in these complexes. Taking the most dramatic example of Cl^-, the pentacoordinate intermediate FeN_4A is more efficiently trapped by Cl^- than by CO. Because Cl^- is strongly trans labilizing for subsequent dissociation of A ($k_{-A}{}^{Cl} \gg k_{-A}{}^{A}$) the minor component, FeN_4ACl^-, reacts with CO much faster than the major component, FeN_4A_2, resulting in the reaction proceeding almost entirely[6] via the Cl^--trapped intermediate.

The ratios of k_2 in Table I afford reasonable estimates of the relative trans effects on A lability. Relative to the previous estimate[3] of 1000 s^{-1} for $k_{-A}{}^{A}$, k_{-A} is approximately 10^7 s^{-1}, 3×10^5 s^{-1}, 8×10^3 s^{-1}, and 44 s^{-1} trans to Br^-, Cl^-, NCS^-, and CN^-, respectively.[7] The trans-effect order on CH_3CN lability correlates with the π-bonding properties of X^- (π-donors labilizing and π-acceptors delabilizing).

The flash photolysis studies of $FeN_4X(CO)^-$ also provide data concerning the kinetics of eq 1. At low $[X^-]$ the initial photoproduct, FeN_4AX^-, undergoes rapid dissociation of X^- (reverse of eq 1) producing an equilibrium mixture of FeN_4A_2 and FeN_4AX^-. These reactions are much faster than those associated with CO ligation described above. For X = Cl^-, an increase in absorbance at 444 nm is observed after the flash independent of [CO] and with a dependence on $[Cl^-]$ expected for the approach to equilibrium (eq 1) from the right. These data are collected in Table I. The rate constant for anion binding calculated from $k_f = K_X k_{-X}$ gives values of 1850 M^{-1} s^{-1} (Cl^-) and 1000 M^{-1} s^{-1} (NCS^-) in the range of rate constants found previously for the binding of neutral ligands.[3] Since the forward rates vary only slightly with the nature of X^-, an estimate K_{Br} of ~0.1 M^{-1} may be made based on the value of k_{-Br} obtained in the flash experiments. The anionic complexes described here differ from Fe(salen)[8] and heme[9] systems, which do not bind CH_3CN or CO and give pentacoordinate high-spin anionic complexes. In contrast, the low-spin FeN_4A_2 complex actually has a lower affinity for anions because a CH_3CN ligand must be displaced in eq 1.

The dramatic effects of anions reported here are relevant to reported CO ligation characteristics of lacunar systems described by Busch[10,11] and provide a simple model for synergistic (or cooperative) effects of ligation in biological systems.

Acknowledgment. Support of the Natural Sciences and Engineering Research Council is gratefully acknowledged.

Registry No. FeN_4A_2, 129194-53-2; $[Et_4N][FeN_4(CN)(CO)]$, 137059-05-3; FeN_4ABr^-, 137059-06-4; FeN_4ACl^-, 137059-07-5; $FeN_4A(NCS)^-$, 137059-08-6; $FeN_4A(CN)^-$, 137059-09-7; $FeN_4Br(CO)^-$, 137059-10-0; $FeN_4Cl(CO)^-$, 137059-11-1; $FeN_4(NCS)CO^-$, 137059-12-2; $FeN_4(CN)CO^-$, 137059-04-2.

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(6) The carbonyl product is a kinetic (not thermodynamic) product under the conditions used. Product spectra are consistent with the amount of $FeN_4A(CO)$ and $FeN_4Cl(CO)^-$ expected based on the relative rates of the k_1 and k_2 paths.

(7) These estimates consider the ratio k_1/k_2 (eqs 6 and 7) and assume k_{+A}/k_{+CO} is independent of the trans ligand.

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Synthesis, Crystal and Molecular Structure, and Magnetic Properties of Bis[(μ-3,5-diamino-1,2,4-triazole-N^1,N^2)bis(μ-3,5-diamino-1,2,4-triazolato-N^1,N^2)triaquacobalt(II)]cobalt(III) Trichloride Nonahydrate

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1,2,4-Triazoles, Rtr, have been actively investigated as ligands capable of giving polymeric compounds with transition-metal ions and of effectively transmitting magnetic interactions between them.[2-9] In particular Reedijk et al. prepared series of trinuclear compounds of general formula $[M_3(Rtr)_6(H_2O)_6]^{6+}$, M = Mn, Fe, Co, Ni, and Zn, where Rtr is a substituted triazole. The exchange interaction has been found to be antiferromagnetic between the nearest-neighbor magnetic ions.[6-8] In these complexes the external ions are different from the internal one, and this allowed Reedijk et al. to observe a high-spin–low-spin transition of the central ion in a linear trinuclear iron(II) triazole compound.[6]

Despite the relatively large number of compounds containing triazoles so far isolated we are not aware of any trinuclear system with mixed-valence characteristics, although this possibility might

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