luminescent levels are reached with unitary efficiency (within an experimental error of ±20%) regardless of the excitation wavelength (in particular, regarding excitation in the ligand-centered bpy band at 282 nm and 2,3-dpp band at 350 nm).

Superamolecular species like **1** are very interesting because they contain many chromophoric and redox centers and exhibit luminescence from relatively long-lived excited states. Because of these properties, they are good candidates to play the roles of photosensitizers,[13-15] luminescent probes,[16,17] and multielectron-transfer catalysts.[18] By using different metals, bridging ligands, or terminal ligands, it is also possible to control the direction of electronic energy migration in supramolecular structures of this type (antenna devices).[2c,f,i,j,15]

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Complexes of Zinc Finger Peptides with Ni^{2+} and Fe^{2+}

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In 1983, it was discovered that the eukaryotic DNA binding protein transcription factor IIIA (TFIIIA) contained bound zinc ions as isolated and that these ions were required for site-specific DNA binding activity.[1] Treatment of the purified protein with EDTA abolished specific DNA binding activity. The activity could be restored by treatment of 15 μM Zn^{2+} but not by the same concentration of Fe^{2+}, Ni^{2+}, Co^{2+}, or Mn^{2+}. Analysis[2,3] of the deduced amino acid sequence of TFIIIA[4] revealed the presence of nine sequences that approximate the form (Phe,Tyr)-X-Cys-$X_{2,4}$-Cys-X_3-Phe-X_5-Leu-X_2-His-$X_{3,4}$-His-X_{2-6} where X represents relatively variable amino acids. It was proposed that each of these sequences binds a zinc ion through the invariant cysteinate and histidine residues to form a structural domain termed a "zinc finger". A variety of evidence has confirmed this hypothesis for TFIIIA.[5] In addition, a large number of other proteins have been found to contain similar sequences, and extant data are consistent with the proposition that these also form metal-based domains.[5,6]

While several studies have been reported concerning the structural and zinc binding properties of single zinc finger peptides,[7-16] the ability of these peptides to act as ligands for other metal ions has not been extensively described. We report that a prototypical zinc finger peptide, CP-1,[17] can indeed bind Ni^{2+} and Fe^{2+} in addition to Co^{2+} to produce complexes whose spectroscopic properties are consistent with distorted tetrahedral coordination by the cysteinate and histidine residues. In addition, studies of the affinity of this peptide for various metal ions reveal that the specificity of a single domain peptide in binding zinc over other metal ions is sufficient to explain the unique ability of zinc to restore the DNA binding activity of TFIIIA under the conditions reported.

Experimental Section

The peptides CP-1 and CP-1(H24C) were prepared and purified as described previously. All experiments were performed in an oxygen-free 98% nitrogen/2% hydrogen atmosphere. Optical spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian XL-400 spectrometer.

Results and Discussion

For these studies, the zinc finger peptide CP-1 which has the sequence ProTyrLys*Cys*ProGlu*Cys*GlyLysSerPheSerGlnLysSerAspLeuValLys*His*GlnArgThr*His*ThrGly was used.[17] This is a consensus peptide based on a large data base of zinc finger sequences. For comparison, the sequence variant CP-1(H24C)-ProTyrLys*Cys*ProGlu*Cys*GlyLysSerPheSerGlnLysSerAspLeuValLys*His*GlnArgThr*Cys*ThrGly was also studied. Previous studies have shown that CP-1 and CP-1(H24C) bind Co^{2+} and Zn^{2+}. The ability of these peptides to bind Cu^{2+}, Ni^{2+}, Fe^{2+}, and Mn^{2+} was investigated spectrophotometrically. Cu^{2+} was found to oxidize the peptides presumably to disulfide-linked species. The absorption spectra of the Ni^{2+} and Fe^{2+} complexes are shown in Figure 1. The spectra of the Ni^{2+} complexes are similar to those observed for distorted Ni^{2+} complexes such as Ni^{2+}-substituted aspartate transcarbamylase[18] and rubredoxin.[19] The ligand field transitions are blue shifted consistent with Ni(imidazole)$_{2,1}$(thiolate)$_{2,3}$ rather than Ni(thiolate)$_4$ chromophores, given the positions of thiolate and imidazole in the spectrochemical series.[20,21] In addition, the bands are somewhat more clearly resolved into components, consistent with the reduction of symmetry of the ligand fields compared with Ni(thiolate)$_4$. Additional ligand field bands were observed in the near infrared with maxima (nm) and extinction coefficients (M^{-1} cm^{-1}, in parentheses) as follows: CP-1(Ni2+), 1600 (15), 1725 (25); CP-1(H24C), 1550 (5), 1700 (10). The spectra of the Fe^{2+} complexes consist predominantly of a set of charge-transfer transitions in the ultraviolet. Examination of the spectra extending into the near-infrared region revealed the presence of bands at 1400–1800 nm with extinction coefficients near 80 M^{-1} cm^{-1}. Again, these features are similar

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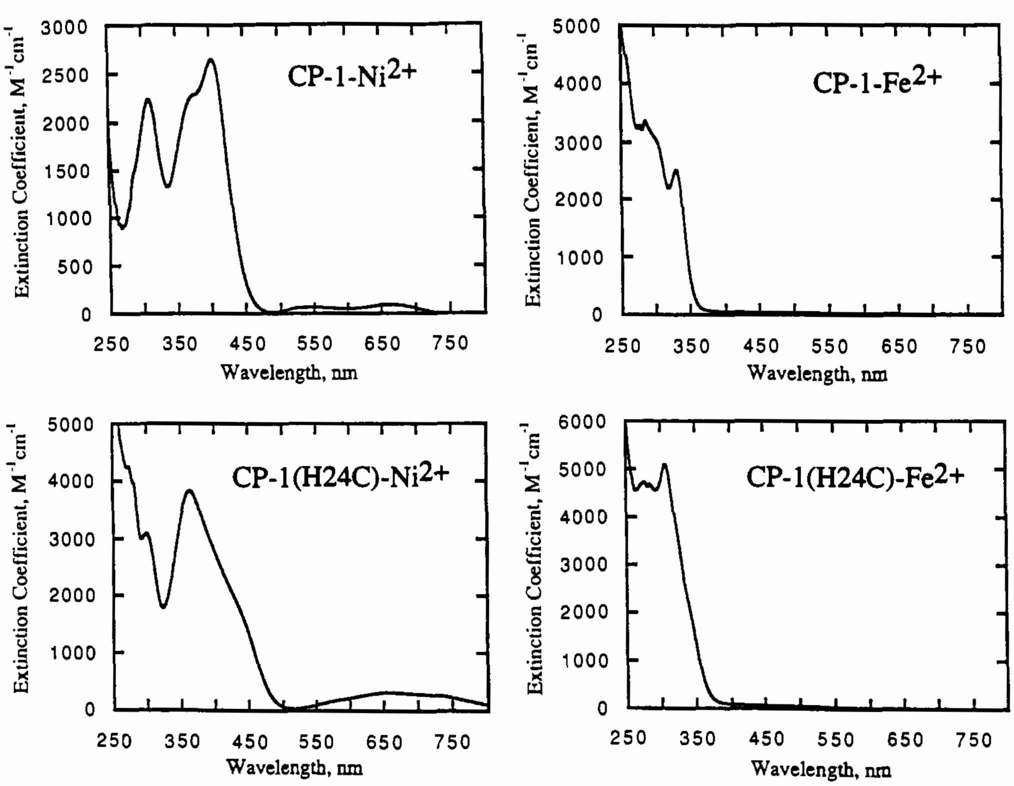

Figure 1. Absorption spectra of CP-1–Ni^{2+}, CP-1–Fe^{2+}, CP-1(H24C)–Ni^{2+}, and CP-1(H24C)–Fe^{2+} in the ultraviolet and visible regions. The spectra have been corrected for peptide absorption. All spectrophotometric experiments were performed in 100 mM HEPES/50 mM NaCl, pH 7.0, buffer.

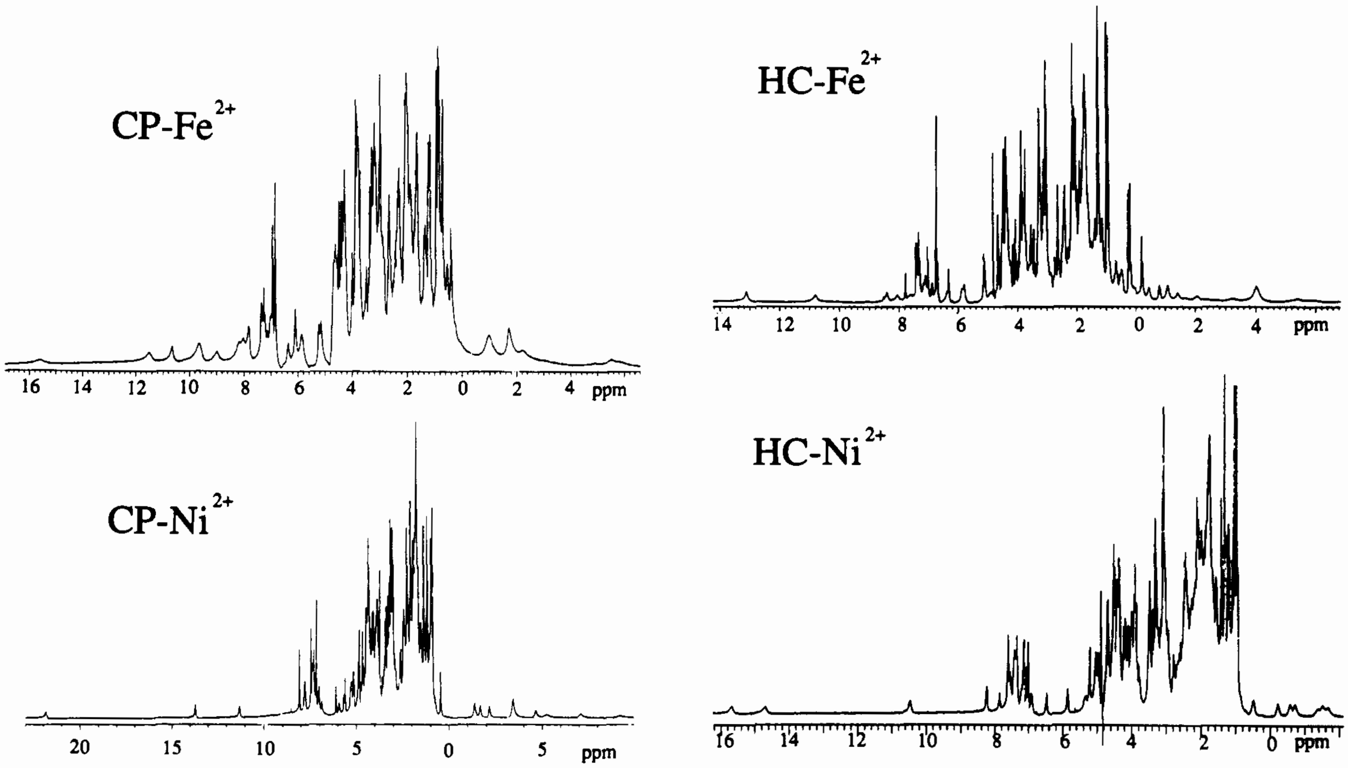

Figure 2. ^{1}H NMR spectra of CP-1–Fe^{2+} (3.3 mM, pH 7.15), CP-1–Ni^{2+} (2.0 mM, pH 7.26), CP-1(H24C)–Fe^{2+} (2.1 mM, pH 7.14), and CP-1(H24C)–Ni^{2+} (1.5 mM, pH 7.20) in D$_2$O.

to tetrahedral ferrous complexes such as that in reduced rubredoxin.[22] Exposing these samples to air resulted in the development of red colors with absorption bands in the visible near 500 nm. This presumably results from the oxidation of the complexes to Fe^{3+} forms. Further characterization of these oxidation reactions and of the related Fe^{3+} complexes is in progress. Addition of 1 equiv of Mn^{2+} to CP-1 produced a set of weak absorption bands in the visible region ($\epsilon < 10$ M^{-1} cm^{-1}). However, further additions produced a band in the edge of the ultraviolet that extended into the visible region, precluding further studies.

Initial ^{1}H NMR studies of the Ni^{2+} and Fe^{2+} complexes of CP-1 and CP-1(H24C) have been performed. Spectra are shown in Figure 2. Numerous paramagnetically shifted resonances are

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observed for all complexes. The large number of shifted resonances indicates that many residues in addition to those directly coordinated to the metal center are affected via dipolar interactions. Further studies will be necessary to assign the spectra and to attempt to locate additional resonances that are more dramatically shifted. Nonetheless, the spectra clearly support the assignment of the Ni^{2+} complexes as paramagnetic and, hence, distorted tetrahedral rather than diamagnetic and square planar. The relatively broad lines of the Fe^{2+} complex are consistent with high-spin d^6 complexes.

The affinities of CP-1 for Ni^{2+} and Fe^{2+} were determined by metal ion titrations similar to those described previously.[8,17] Fitting the results of these experiments revealed dissociation constants (with estimated standard deviations in parentheses) of $K_d^{Ni} = 1.6$ (± 0.9) $\times 10^{-6}$ M and $K_d^{Fe} = 2.5$ (± 0.8) $\times 10^{-6}$ M for CP-1 and $K_d^{Ni} = 1.2$ (± 0.4) $\times 10^{-6}$ M and $K_d^{Fe} = 2.4$ (± 0.8) $\times 10^{-6}$ M for CP-1(H24C). Competition experiments with Co^{2+}, Fe^{2+}, and Ni^{2+} with CP-1 suggested that $K_d^{Mn} > 10^{-5}$ M. Zn^{2+}, which binds to CP-1 with $K_d^{Zn} = 2 \times 10^{-12}$,[17] is bound 6 to 9 kcal/mol more tightly than are the other metal ions. The trends in these values are somewhat reminiscent of the corresponding trends for formation of a series of MCl_4^{2-} ions.[23] This behavior has been interpreted in terms of changes in ligand field stabilization energy being a significant component in determining the heats of formation although other factors are also important. The relative ion affinities we have observed indicate that the specific reactivation of TFIIIA by zinc can be accounted for by metal ion affinity without requiring any significant structural differences in the metal complexes once they are formed. Moreover, these initial observations reveal that zinc finger peptides such as CP-1 and CP-1-(H24C) should be useful in studying the properties of a variety of metal ions in distorted tetrahedral mixed sulfur–nitrogen coordination environments.

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Reactions of Tellurium Halides with Sulfur *N,N'*-Bis(trimethylsilyl)diimide—Preparation of the First Fluorotellurium Nitride

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Introduction

The use of sulfur diimides as versatile synthetic reagents in sulfur–nitrogen chemistry is well documented.[1] In addition, they have been found to be excellent precursors in synthesizing novel transition-metal-containing heterocycles.[2] Recently, we reported on the synthesis of $(ClTeNSN)_3N$, the first example of a tellurium nitride stable at room temperature, from reaction of tellurium(IV) chloride with sulfur *N,N'*-bis(trimethylsilyl)diimide (**1**).[3] Herein we report the synthesis and X-ray structural characterization of $(FTeNSN)_3N$ (**2**) using a similar synthetic route involving **1** and tellurium(IV) fluoride.

Experimental Section

Experimental manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried according to standard methods. Tellurium(IV) fluoride[4] and sulfur *N,N'*-bis(trimethylsilyl)diimide[5] (**1**) were prepared by known methods.

For the ^{19}F NMR spectrum $CFCl_3$ was used as an external standard. The ^{125}Te NMR spectrum was determined at ambient temperature with Me_2Te as an external standard. The IR spectrum was obtained as a Nujol mull between sodium chloride windows. Only strong (s) and very strong (vs) bands are reported.

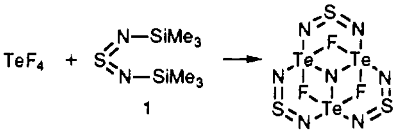
Crystal Data for 2·2(pyridine): $C_{10}H_{10}F_3N_9S_3Te_3$, MW = 792.3, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.848$ (2) Å, $b = 10.040$ (3) Å, $c = 12.598$ (3) Å, $\alpha = 69.15$ (1)°, $\beta = 82.99$ (2)°, $\gamma = 68.73$ (1)°, $V = 974.6$ (4) $Å^3$, $Z = 2$, $\rho_{calcd} = 2.700$ Mg m^{-3}, $\mu = 4.83$ mm^{-1}, crystal dimensions $0.2 \times 0.3 \times 0.4$ mm. The X-ray structure determination was carried out on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 4516 reflections was measured at −120 °C with a profile-fitting method for $2\theta < 55°$. A semiempirical absorption correction was applied. After equivalents were merged, 4294 independent data with $F > 4\sigma(F)$ were used for all calculations. The structure was solved by Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. A riding model with idealized hydrogen geometry was employed for H-atom refinement. The full-matrix least-squares refinement converged to final residues $R(F_o) = 0.0216$, $R_w(F_o) = 0.0245$ with $w^{-1} = \sigma^2(F) + 0.0001F^2$. All calculations were performed with SHELXS[6] and SHELXTL.

Caution: Compound **2** may decompose violently when exposed to mechanical strain!

To a suspension of 0.94 g (4.6 mmol) of tellurium(IV) fluoride in ether (30 mL) was added dropwise at ambient temperature a solution of 1.04 g (5.1 mmol) of **1** in the same solvent (30 mL). A white precipitate was formed instantaneously. When the reaction mixture was stirred for another 8 h, the color of the precipitate was found to turn to red. The solid was filtered off, redissolved in pyridine/toluene (3:1) and allowed to crystallize at −10 °C, giving 0.50 g (0.8 mmol) of **2** (51%) after drying in vacuo. Recrystallization from the same solvent mixture gave crystals suitable for X-ray structure determination. Mp: 112 °C dec. IR spectrum: 1205 (s), 1149 (vs), 1056 (vs) cm^{-1}. ^{19}F NMR (pyridine-/C_6D_6): −42.6 ppm (s). ^{125}Te NMR (pyridine/C_6D_6): 1157 ppm. Anal. Calcd for **2**, $F_3N_7S_3Te_3$: N, 15.46; F, 9.0. Found: N, 14.7; F, 10.6.

Results and Discussion

A reaction of tellurium(IV) fluoride with a slight excess of sulfur *N,N'*-bis(trimethylsilyl)diimide (**1**) in ether at room temperature proceeds readily with the formation of the novel tellurium nitride **2**.



1 **2**

During the reaction, initially the formation of a white precipitate is observed, which on stirring for some time turns red. To investigate whether the white solid might be an intermediate, this reaction was carried out again at −5 °C and stirred for only 30 min. The white solid was filtered off. A comparison of the IR spectra of the red and white reaction products showed identical absorptions due to the NSN units as broad absorption bands (1149 and 1056 cm^{-1}).

The ^{19}F NMR chemical shift of compound **2** was found about 17 ppm higher than the signal reported for tellurium(IV) fluoride.[7] No ^{125}Te satellites have been observed. However, no attempt was made to detect such couplings by recording the spectrum at lower temperature. The ^{125}Te NMR spectrum shows a very broad signal ($\Delta\nu_{1/2} = 505$ Hz, 1157 ppm). The shift of the analogous chloride $(ClTeNSN)_3N$ in the same solvent was found at 1212 ppm.[8] No coupling with the directly bonded F atoms is observed, indicating

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